



(11) **EP 2 420 546 B2**

(12) **NEW EUROPEAN PATENT SPECIFICATION**
After opposition procedure

(45) Date of publication and mention
of the opposition decision:
08.04.2020 Bulletin 2020/15

(51) Int Cl.:
C09K 5/04 (2006.01)

(45) Mention of the grant of the patent:
26.04.2017 Bulletin 2017/17

(21) Application number: **11189771.6**

(22) Date of filing: **31.08.2007**

(54) **Terephthalate stabilizers for fluoroolefins**

Terephthalatstabilisierer für Fluorolefine

Stabilisateurs de téréphtalate pour fluoroléfines

(84) Designated Contracting States:
DE ES FR GB IT

(30) Priority: **01.09.2006 US 841947 P**
01.09.2006 US 841977 P
01.09.2006 US 841839 P
01.09.2006 US 841882 P

(43) Date of publication of application:
22.02.2012 Bulletin 2012/08

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
07811630.8 / 2 057 247

(73) Proprietor: **The Chemours Company FC, LLC**
Wilmington DE 19801 (US)

(72) Inventors:
• **Leck, Thomas J.**
Hockessin, DE 19707 (US)

- **Minor, Barbara Haviland**
Elkton, MD 21921 (US)
- **Nappa, Mario Joseph**
Leesburg, FL 34748 (US)
- **Mouli, Nandini**
Reisterstown, MD 21136 (US)
- **Howell, Jon Lee**
Bear, DE 19701 (US)

(74) Representative: **Dehns**
St. Bride's House
10 Salisbury Square
London EC4Y 8JD (GB)

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Description**BACKGROUND OF THE INVENTION**

1. Field of the Invention.

[0001] The present invention relates to compositions comprising at least one fluoroolefin and a stabilizer comprising at least one terephthalate or a mixture thereof with ascorbic acid or nitromethane. The stabilized compositions may be useful in cooling systems as replacements for existing working fluids with higher global warming potential. 2. Description of Related Art.

[0002] New environmental regulations on working fluids have forced the refrigeration and air-conditioning industry to look for new working fluids with low global warming potential (GWP).

[0003] Replacement working fluids are being sought that have low GWP, no toxicity, non-flammability, reasonable cost and excellent refrigeration performance.

[0004] Fluoroolefins have been proposed as working fluids alone or in mixtures. However, it has been observed that fluoroolefins can exhibit degradation when exposed to high temperatures or when contacted with other compounds (e.g., moisture, oxygen, or other compounds with which they may undergo condensation reactions. This degradation may occur when fluoroolefins are used as working fluids in heat transfer equipment (refrigeration or air-conditioning equipment, for instance) or when used in some other application. This degradation may occur by any number of different mechanisms. In one instance, the degradation may be caused by instability of the compounds at extreme temperatures. The use of stabilisers has been reported as a possible route to reduce this cause of degradation - see, for example, U.S. Published Patent Application No. 2006/033072. In other instances, the degradation may be caused by oxidation in the presence of air that has inadvertently leaked into the system. Whatever the cause of such degradation, because of the instability of the fluoroolefins, it may not be practical to incorporate these fluoroolefins into refrigeration or air-conditioning systems. Therefore, to take advantage of the many other attributes of fluoroolefins, means to reduce the degradation is needed.

SUMMARY OF THE INVENTION

[0005] To avoid possible instability of the fluoroolefins at the extremes of system operation (especially at high temperatures), it has been found that adding specific compounds, namely at least one terephthalate selected from divinyl terephthalate and diphenyl terephthalate, or a mixture thereof with at least one of ascorbic acid and nitromethane, to fluoroolefins will increase the stability thereof in refrigeration or air-conditioning system applications.

[0006] Therefore, in accordance with the present invention, there is provided a composition comprising at least one fluoroolefin and an effective amount of a stabilizer comprising at least one terephthalate selected from divinyl terephthalate and diphenyl terephthalate.

[0007] Also provided is a method for stabilizing a composition comprising at least one fluoroolefin, said method comprising adding an effective amount of a stabilizer comprising at least one at least one terephthalate selected from divinyl terephthalate and diphenyl terephthalate to the composition comprising at least one fluoroolefin.

[0008] Also provided is a method for reducing degradation of a composition comprising at least one fluoroolefin, wherein said degradation is caused by the presence of inadvertent air in a refrigeration, air-conditioning or heat pump system, said method comprising adding an effective amount of a stabilizer comprising at least one at least one terephthalate selected from divinyl terephthalate and diphenyl terephthalate to the composition comprising at least one fluoroolefin.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The present invention provides a composition comprising at least one fluoroolefin and an effective amount of a stabilizer comprising at least one at least one terephthalate selected from divinyl terephthalate and diphenyl terephthalate.

[0010] These compositions have a variety of utilities in working fluids, which include blowing agents, solvents, aerosol propellants, fire extinguishants, sterilants or heat transfer mediums (such as heat transfer fluids and refrigerants for use in refrigeration systems, refrigerators, air conditioning systems, heat pumps, chillers, and the like), to name a few.

[0011] A blowing agent is a volatile composition that expands a polymer matrix to form a cellular structure.

[0012] A solvent is a fluid that removes a soil from a substrate, or deposits a material onto a substrate, or carries a material.

[0013] An aerosol propellant is a volatile composition of one or more components that exerts a pressure greater than one atmosphere to expel a material from a container.

[0014] A fire extinguishant is a volatile composition that extinguishes or suppresses a flame.

[0015] A sterilant is a volatile biocidal fluid or blend containing a volatile biocidal fluid that destroys a biologically active material or the like.

[0016] A heat transfer medium (also referred to herein as a heat transfer fluid, a heat transfer composition or a heat transfer fluid composition) is a working fluid used to carry heat from a heat source to a heat sink.

[0017] A refrigerant is a compound or mixture of compounds that function as a heat transfer fluid in a cycle wherein the fluid undergoes a phase change from a liquid to a gas and back.

[0018] The term fluoroolefins, as used herein, describes compounds which comprise carbon atoms, fluorine atoms, and optionally hydrogen atoms. In one embodiment, the fluoroolefins used in the compositions of the present invention comprise compounds with 2 to 12 carbon atoms. In another embodiment the fluoroolefins comprise compounds with 3 to 10 carbon atoms, and in yet another embodiment the fluoroolefins comprise compounds with 3 to 7 carbon atoms. Representative fluoroolefins include but are not limited to all compounds as listed in Table 1, Table 2, and Table 3.

[0019] One embodiment of the present invention provides fluoroolefins having the formula E - or Z - $R^1CH=CHR^2$ (Formula I), wherein R^1 and R^2 are, independently, C_1 to C_6 perfluoroalkyl groups. Examples of R^1 and R^2 groups include, but are not limited to, CF_3 , C_2F_5 , $CF_2CF_2CF_3$, $CF(CF_3)_2$, $CF_2CF_2CF_2CF_3$, $CF(CF_3)CF_2CF_3$, $CF_2CF(CF_3)_2$, $C(CF_3)_3$, $CF_2CF_2CF_2CF_2CF_3$, $CF_2CF_2CF(CF_3)_2$, $C(CF_3)_2C_2F_5$, $CF_2CF_2CF_2CF_2CF_2CF_3$, $CF(CF_3)CF_2CF_2C_2F_5$, and $C(CF_3)_2CF_2C_2F_5$. In one embodiment the fluoroolefins of Formula I have at least about 4 carbon atoms in the molecule. In another embodiment, the fluoroolefins of Formula I have at least about 5 carbon atoms in the molecule. Exemplary, non-limiting Formula I compounds are presented in Table 1.

TABLE 1

Code	Structure	Chemical Name
F11E	$CF_3CH=CHCF_3$	1,1,1,4,4,4-hexafluorobut-2-ene
F12E	$CF_3CH=CHC_2F_5$	1,1,1,4,4,5,5,5-octafluoropent-2-ene
F13E	$CF_3CH=CHCF_2C_2F_5$	1,1,1,4,4,5,5,8,6,6-decafluorohex-2-ene
F13iE	$CF_3CH=CHCF(CF_3)_2$	1,1,1,4,5,5,5-heptafluoro-4-(trifluoromethyl)pent-2-ene
F22E	$C_2F_5CH=CHC_2F_5$	1,1,1,2,2,3,5,5,6,6,6-decafluorohex-3-ene
F14E	$CF_3CH=CH(CF_2)_3CF_3$	1,1,1,4,4,5,5,6,6,7,7,7-dodecafluorohept-2-ene
F14iE	$CF_3CH=CHCF_2CF(CF_3)_2$	1,1,1,4,4,5,6,6,6-nonafluoro-5-(trifluoromethyl)hex-2-ene
F14sE	$CF_3CH=CHCF(CF_3)-C_2F_6$	1,1,1,4,5,5,6,6,6-nonfluoro-4-(trifluoromethyl)hex-2-ene
F14tE	$CF_3CH=CHC(CF_3)_3$	1,1,1,5,5,5-hexafluoro-4,4-bis(trifluoromethyl)pent-2-ene
F23E	$C_2F_5CH=CHCF_2C_2F_5$	1,1,1,2,2,5,5,6,6,7,7,7-dodecafluorohept-3-ene
F23iE	$C_2F_5CH=CHCF(CF_3)_2$	1,1,1,2,2,5,6,6,6-nonafluoro-5-(trifluoromethyl)hex-3-ene
F15E	$CF_3CH=CH(CF_2)_4CF_3$	1,1,1,4,4,5,5,6,5,7,7,8,8,8-tetradecafluorooct-2-ene
F15iE	$CF_3CH=CH-CF_2CF_2CF(CF_3)_2$	1,1,1,4,4,5,5,6,7,7,7-undecafluoro-6-(trifluoromethyl)hept-2-ene
F15tE	$CF_3CH=CH-C(CF_3)_2C_2F_5$	1,1,1,5,5,6,6,6-octafluoro-4,4-bis(trifluoromethyl)hex-2-ene
F24E	$C_2F_5CH=CH(CF_2)_3CF_3$	1,1,1,2,2,5,5,6,6,7,7,8,8,8-tetradecafluorooct-3-ene
F24iE	$C_2F_5CH=CHCF_2CF(CF_3)_2$	1,1,1,2,2,5,5,6,7,7,7-undecafluoro-6-(trifluoromethyl)hept-3-ene
F24sE	$C_2F_5CH=CHCF(CF_3)-C_2F_5$	1,1,1,2,2,5,6,6,7,7,7-undecafluoro-5-(trifluoromethyl)hept-3-ene
F24tE	$C_2F_5CH=CHC(CF_3)_3$	1,1,1,2,2,6,6,6-octafluoro-5,5-bis(trifluoromethyl)hex-3-ene
F33E	$C_2F_5CF_2CH=CH-CF_2C_2F_5$	1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluorooct-4-ene
F33iE	$(CF_3)_2CFCH=CH-CF(CF_3)_2$	1,1,1,2,5,6,6,6-octafluoro-2,5-bis(trifluoromethyl)hex-3-ene
F33iE	$C_2F_5CF_2CH=CH-CF(CF_3)_2$	1,1,1,2,5,5,6,6,7,7,7-undecafluoro-2-(trifluoromethyl)hept-3-ene
F16E	$CF_3CH=CH(CF_2)_5CF_3$	1,1,1,4,4,5,5,6,6,7,7,8,8,9,9,9-hexadecafluoronon-2-ene
F16sE	$CF_3CH=CHCF(CF_3)(CF_2)_2C_2F_5$	1,1,1,4,5,5,6,6,7,7,8,8,8-tridecafluoro-4-(trifluoromethyl)hept-2-ene
F16tE	$CF_3CH=CHC(CF_3)_2CF_2C_2F_5$	1,1,1,6,6,6-octafluoro-4,4-bis(trifluoromethyl)hept-2-ene

(continued)

	Code	Structure	Chemical Name
5	F25E	$C_2F_5CH=CH(CF_2)_4CF_3$	1,1,1,2,2,5,5,6,6,7,7,8,8,9,9-hexadecafluoronon-3-ene
	F25iE	$C_2F_5CH=CH-CF_2CF_2CF(CF_3)_2$	1,1,1,2,2,5,5,6,6,7,7,8,8,8-tridecafluoro-7-(trifluoromethyl)oct-3-ene
	F25tE	$C_2F_5CH=CH-C(CF_3)_2C_2F_5$	1,1,1,2,2,6,6,7,7,7-decafluoro-5,5-bis(trifluoromethyl)hept-3-ene
10	F34E	$C_2F_5CF_2CH=CH-(CF_2)_3CF_3$	1,1,1,2,2,3,3,6,6,7,7,8,8,9,9-hexadecafluoronon-4-ene
	F34iE	$C_2F_5CF_2CH=CH-CF_2CF(CF_3)_2$	1,1,1,2,2,3,3,6,6,7,7,8,8,8-tridecafluoro-7-(trifluoromethyl)oct-4-ene
15	F34sE	$C_2F_5CF_2CH=CH-CF(CF_3)C_2F_6$	1,1,1,2,2,3,3,6,6,7,7,8,8,8-tridecafluoro-6-(trifluoromethyl)oct-4-ene
	F34tE	$C_2F_5CF_2CH=CH-C(CF_3)_3$	1,1,1,5,5,6,6,7,7,7-decafluoro-2,2-bis(trifluoromethyl)hept-3-ene
	F3i4E	$(CF_3)_2CFCH=CH-(CF_2)_3CF_3$	1,1,1,2,5,5,6,6,7,7,8,8,8-tridecafluoro-2(trifluoromethyl)oct-3-ene
	F3i4iE	$(CF_3)_2CFCH=CH-CF_2CF(CF_3)_2$	1,1,1,2,5,5,6,6,7,7,7-decafluoro-2,6-bis(trifluoromethyl)hept-3-ene
20	F3i4sE	$(CF_3)_2CFCH=CH-CF(CF_3)C_2F_5$	1,1,1,2,5,6,6,7,7,7-decafluoro-2,5-bis(trifluoromethyl)hept-3-ene
	F3i4tE	$(CF_3)_2CFCH=CH-C(CF_3)_3$	1,1,1,2,6,6,6-heptafluoro-2,5,5-tris(trifluoromethyl)hex-3-ene
	F26E	$C_2F_5CH=CH(CF_2)_5CF_3$	1,1,1,2,2,5,5,6,6,7,7,8,8,9,9,10,10,10-octadecafluorodec-3-ene
25	F26sE	$C_2F_5CH=CHCF(CF_3)(CF_2)_2C_2F_5$	1,1,1,2,2,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-5-(trifluoromethyl)non-3-ene
	F26tE	$C_2F_5CH=CHC(CF_3)_2CF_2C_2F_5$	1,1,1,2,2,6,6,7,7,8,8,8-dodecafluoro-5,5-bis(trifluoromethyl)oct-3-ene
30	F35E	$C_2F_5CF_2CH=CH-(CF_2)_4CF_3$	1,1,1,2,2,3,3,6,6,7,7,8,8,9,9,10,10,10-octadecafluorodec-4-ene
	F35iE	$C_2F_5CF_2CH=CH-CF_2CF_2CF(CF_3)_2$	1,1,1,2,2,3,3,6,6,7,7,8,8,9,9,9-pentadecafluoro-8-(trifluoromethyl)non-4-ene
	F35tE	$C_2F_5CF_2CH=CH-C(CF_3)_2C_2F_5$	1,1,1,2,2,3,3,7,7,8,8,8-dodecafluoro-6,6-bis(trifluoromethyl)oct-4-ene
35	F3i5E	$(CF_3)_2CFCH=CH-(CF_2)_4CF_3$	1,1,1,2,5,5,6,6,7,7,8,6,9,9,9-pentadecafluoro-2-(trifluoromethyl)non-3-ene
	F3i5iE	$(CF_3)_2CFCH=CH-CF_2CF_2CF(CF_3)_2$	1,1,1,2,5,5,6,6,7,7,8,8,8-dodecafluoro-1,7-bis(trifluoromethyl)oct-3-ene
40	F3i5tE	$(CF_3)_2CFCH=CH-C(CF_3)_2C_2F_5$	1,1,1,2,6,6,7,7,7-nonafluoro-2,5,5-tris(trifluoromethyl)hept-3-ene
	F44E	$CF_3(CF_2)_3CH=CH-(CF_2)_3CF_3$	1,1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10,10-octadecafluorodec-5-ene
45	F44iE	$CF_3(CF_2)_3CH=CH-CF_2CF(CF_3)_2$	1,1,1,2,3,3,6,6,7,7,8,8,9,9,9-pentadecafluoro-2-(trifluoromethyl)non-4-ene
	F44sE	$CF_3(CF_2)_3CH=CH-CF(CF_3)C_2F_5$	1,1,1,2,2,3,6,6,7,7,8,8,9,9,9-pentadecafluoro-3-(trifluoromethyl)non-4-ene
	F44tE	$CF_3(CF_2)_3CH=CH-C(CF_3)_3$	1,1,1,5,5,6,6,7,7,8,8,8-dodecafluoro-2,2-bis(trifluoromethyl)oct-3-ene
50	F4i4iE	$(CF_3)_2CFCF_2CH=CH-CF_2CF(CF_3)_2$	1,1,1,2,3,3,6,6,7,7,8,8,8-dodecafluoro-2,7-bis(trifluoromethyl)oct-4-ene
	F4i4sE	$(CF_3)_2CFCF_2CH=CH-CF(CF_3)C_2F_5$	1,1,1,2,3,3,6,7,7,8,8,8-dodecafluoro-2,6-bis(trifluoromethyl)oct-4-ene
55	F4i4tE	$(CF_3)_2CFCF_2CH=CH-C(CF_3)_3$	1,1,1,5,5,6,7,7,7-nonafluoro-2,2,6-tris(trifluoromethyl)hept-3-ene

(continued)

Code	Structure	Chemical Name
F4s4sE	$C_2F_5CF(CF_3)CH=CH-CF(CF_3)C_2F_5$	1,1,1,2,2,3,6,7,7,8,8,8-dodecafluoro-3,6-bis(trifluoromethyl)oct-4-ene
F4s4tE	$C_2F_5CF(CF_3)CH=CH-C(CF_3)_3$	1,1,1,5,6,6,7,7,7-nonafluoro-2,2,5-tris(trifluoromethyl)hept-3-ene
F4t4tE	$(CF_3)_3CCH=CH-C(CF_3)_3$	1,1,1,6,6,6-hexafluoro-2,2,5,5-tetrakis(trifluoromethyl)hex-3-ene

[0020] Compounds of Formula I may be prepared by contacting a perfluoroalkyl iodide of the formula R^1I with a perfluoroalkyltriiodoperfluoroalkene of the formula $R^2CH=CH_2$ to form a triiodoperfluoroalkane of the formula $R^1CH_2CHIR^2$. This triiodoperfluoroalkane can then be deiodinated to form $R^1CH=CHR^2$. Alternatively, the olefin $R^1CH=CHR^2$ may be prepared by deiodination of a triiodoperfluoroalkane of the formula $R^1CHICH_2R^2$ formed in turn by reacting a perfluoroalkyl iodide of the formula R^2I with a perfluoroalkyltriiodoperfluoroalkene of the formula $R^1CH=CH_2$.

[0021] The contacting of a perfluoroalkyl iodide with a perfluoroalkyltriiodoperfluoroalkene may take place in batch mode by combining the reactants in a suitable reaction vessel capable of operating under the autogenous pressure of the reactants and products at reaction temperature. Suitable reaction vessels include fabricated from stainless steels, in particular of the austenitic type, and the well-known high nickel alloys such as Monel® nickel-copper alloys, Hastelloy® nickel based alloys and Inconel® nickel-chromium alloys.

[0022] Alternatively, the reaction may take be conducted in semi-batch mode in which the perfluoroalkyltriiodoperfluoroalkene reactant is added to the perfluoroalkyl iodide reactant by means of a suitable addition apparatus such as a pump at the reaction temperature.

[0023] The ratio of perfluoroalkyl iodide to perfluoroalkyltriiodoperfluoroalkene should be between about 1:1 to about 4:9, preferably from about 1.5:1 to 2.5:1. Ratios less than 1.5:1 tend to result in large amounts of the 2:1 adduct as reported by Jeanneaux, et. al. in Journal of Fluorine Chemistry, Vol. 4, pages 261-270 (1974).

[0024] Preferred temperatures for contacting of said perfluoroalkyl iodide with said perfluoroalkyltriiodoperfluoroalkene are preferably within the range of about 150°C to 300°C, preferably from about 170°C to about 250°C, and most preferably from about 180°C to about 230°C. Suitable contact times for the reaction of the perfluoroalkyl iodide with the perfluoroalkyltriiodoperfluoroalkene are from about 0.5 hour to 18 hours, preferably from about 4 to about 12 hours.

[0025] The triiodoperfluoroalkane prepared by reaction of the perfluoroalkyl iodide with the perfluoroalkyltriiodoperfluoroalkene may be used directly in the deiodination step or may preferably be recovered and purified by distillation prior to the deiodination step.

[0026] The deiodination step is carried out by contacting the triiodoperfluoroalkane with a basic substance. Suitable basic substances include alkali metal hydroxides (e.g., sodium hydroxide or potassium hydroxide), alkali metal oxide (for example, sodium oxide), alkaline earth metal hydroxides (e.g., calcium hydroxide), alkaline earth metal oxides (e.g., calcium oxide), alkali metal alkoxides (e.g., sodium methoxide or sodium ethoxide), aqueous ammonia, sodium amide, or mixtures of basic substances such as soda lime. Preferred basic substances are sodium hydroxide and potassium hydroxide. Said contacting of the triiodoperfluoroalkane with a basic substance may take place in the liquid phase preferably in the presence of a solvent capable of dissolving at least a portion of both reactants. Solvents suitable for the deiodination step include one or more polar organic solvents such as alcohols (e.g., methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, and tertiary butanol), nitriles (e.g., acetonitrile, propionitrile, butyronitrile, benzonitrile, or adiponitrile), dimethyl sulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide, or sulfolane. The choice of solvent may depend on the boiling point product and the ease of separation of traces of the solvent from the product during purification. Typically, ethanol or isopropanol are good solvents for the reaction.

[0027] Typically, the deiodination reaction may be carried out by addition of one of the reactants (either the basic substance or the triiodoperfluoroalkane) to the other reactant in a suitable reaction vessel. Said reaction may be fabricated from glass, ceramic, or metal and is preferably agitated with an impeller or stirring mechanism.

[0028] Temperatures suitable for the deiodination reaction are from about 10°C to about 100°C, preferably from about 20°C to about 70°C. The deiodination reaction may be carried out at ambient pressure or at reduced or elevated pressure. Of note are deiodination reactions in which the compound of Formula I is distilled out of the reaction vessel as it is formed.

[0029] Alternatively, the deiodination reaction may be conducted by contacting an aqueous solution of said basic substance with a solution of the triiodoperfluoroalkane in one or more organic solvents of lower polarity such as an alkane (e.g., hexane, heptane, or octane), aromatic hydrocarbon (e.g., toluene), halogenated hydrocarbon (e.g., methylene chloride, chloroform, carbon tetrachloride, or perchloroethylene), or ether (e.g., diethyl ether, methyl tert-butyl ether, tetrahydrofuran, 2-methyl tetrahydrofuran, dioxane, dimethoxyethane, diglyme, or tetraglyme) in the presence of a phase transfer catalyst. Suitable phase transfer catalysts include quaternary ammonium halides (e.g., tetrabutylam-

monium bromide, tetrabutylammonium hydrosulfate, triethylbenzylammonium chloride, dodecyltrimethylammonium chloride, and tricaprylmethylammonium chloride), quaternary phosphonium halides (e.g., triphenylmethylphosphonium bromide and tetraphenylphosphonium chloride), or cyclic polyether compounds known in the art as crown ethers (e.g., 18-crown-6 and 15-crown-5).

[0030] Alternatively, the dehydroiodination reaction may be conducted in the absence of solvent by adding the trihydroiodoperfluoroalkane to a solid or liquid basic substance.

[0031] Suitable reaction times for the dehydroiodination reactions are from about 15 minutes to about six hours or more depending on the solubility of the reactants. Typically the dehydroiodination reaction is rapid and requires about 30 minutes to about three hours for completion.

[0032] The compound of Formula I may be recovered from the dehydroiodination reaction mixture by phase separation after addition of water, by distillation, or by a combination thereof.

[0033] In another embodiment of the present invention, fluoroolefins comprise cyclic fluoroolefins (cyclo-[CX=CY(CZW)_n]) (Formula II), wherein X, Y, Z, and W are independently selected from H and F, and n is an integer from 2 to 5). In one embodiment the fluoroolefins of (Formula II, have at least about 3 carbon atoms in the molecule. In another embodiment, the fluoroolefins of Formula II have at least about 4 carbon atoms in the molecule. In yet another embodiment, the fluoroolefins of Formula II have at least about 5 carbon atoms in the molecule. Representative cyclic fluoroolefins of Formula II are listed in Table 2.

TABLE 2

Cyclic fluoroolefins	Structure	Chemical name
FC-C1316cc	cyclo-CF ₂ CF ₂ CF=CF-	1,2,3,3,4,4-hexafluorocyclobutene
HFC-C1334cc	cyclo-CF ₂ CF ₂ CH=CH-	3,3,4,4-tetrafluorocyclobutene
HFC-C1436	cyclo-CF ₂ CF ₂ CF ₂ CH=CH-	3,3,4,4,5,5-hexafluorocyclopentene
FC-C1418y	cyclo-CF ₂ CF=CFCF ₂ CF ₂ -	1,2,3,3,4,4,5,5-octafluorocyclopentene
FC-C151-10y	cyclo-CF ₂ CF=CFCF ₂ CF ₂ CF ₂ -	1,2,3,3,4,4,5,5,6,6-decafluorocyclohexene

[0034] The compositions of the present invention may comprise a single compound of Formula I or Formula II, for example, one of the compounds in Table 1 or Table 2, or may comprise a combination of compounds of Formula I or Formula II.

[0035] In another embodiment, fluoroolefins may comprise those compounds listed in Table 3.

TABLE 3:

Name	Structure	Chemical name
HFC-1225ye	CF ₃ CF=CHF	1,2,3,3,3-pentafluoro-1-propene
HFC-1225zc	CF ₃ CH=CF ₂	1,1,3,3,3-pentafluoro-1-propene
HFC-1225yc	CHF ₂ CF=CF ₂	1,1,2,3,3-pentafluoro-1-propene
HFC-1234ye	CHF ₂ CF=CHF	1,2,3,3-tetrafluoro-1-propene
HFC-1234yf	CF ₃ CF=CH ₂	2,3,3,3-tetrafluoro-1-propene
HFC-1234ze	CF ₃ CH=CHF	1,3,3,3-tetrafluoro-1-propene
HFC-1234yc	CH ₂ FCF=CF ₂	1,1,2,3-tetrafluoro-1-propene
HFC-1234zc	CHF ₂ CH=CF ₂	1,1,3,3-tetrafluoro-9-propene
HFC-1243yf	CHF ₂ CF=CH ₂	2,3,3-trifluoro-1-propene
HFC-1243zf	CF ₃ CH=CH ₂	3,3,3-trifluoro-1-propene
HFC-1243yc	CH ₃ CF=CF ₂	1,1,2-trifluoro-1-propene
HFC-1243zc	CH ₂ FCH=CF ₂	1,1,3-trifluoro-1-propene
HFC-1243ye	CH ₂ FCF=CHF	1,2,3-trifluoro-1-propene
HFC-1243ze	CHF ₂ CH=CHF	1,3,3-trifluoro-1-propene

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(continued)

	Name	Structure	Chemical name
5	FC-1318my	$\text{CF}_3\text{CF}=\text{CFCF}_3$	1,1,1,2,3,4,4,4-octafluoro-2-butene
	FC-1318cy	$\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2$	1,1,2,3,3,4,4,4-octafluoro-1-butene
	HFC-1327my	$\text{CF}_3\text{CF}=\text{CHCF}_3$	1,1,1,2,4,4,4-heptafluoro-2-butene
	HFC-9 327ye	$\text{CHF}=\text{CFCF}_2\text{CF}_3$	1,2,3,3,4,4,4-heptafluoro-1-butene
10	HFC-1327py	$\text{CHF}_2\text{CF}=\text{CFCF}_3$	1,1,1,2,3,4,4-heptafluoro-2-butene
	HFC-1327et	$(\text{CF}_3)_2\text{C}=\text{CHF}$	1,3,3,3-tetrafluoro-2-(trifluoromethyl)-1-propene
	HFC-1327cz	$\text{CF}_2=\text{CHCF}_2\text{CF}_3$	1,1,3,3,4,4,4-heptafluoro-1-butene
15	HFC-1327cye	$\text{CF}_2=\text{CFCHFCF}_3$	1,1,2,3,4,4,4-heptafluoro-7-butene
	HFC-1327cyc	$\text{CF}_2=\text{CFCF}_2\text{CHF}_2$	1,1,2,3,3,4,4-heptafluoro-1-butene
	HFC-1336yf	$\text{CF}_3\text{CF}_2\text{CF}=\text{CH}_2$	2,3,3,4,4,4-hexafluoro-1-butene
	HFC-1336ze	$\text{CHF}=\text{CHCF}_2\text{CF}_3$	1,3,3,4,4,4-hexafluoro-1-butene
20	HFC-1336eye	$\text{CHF}=\text{CFCHFCF}_3$	1,2,3,4,4,4-hexafluoro-1-butene
	HFC-1336eyc	$\text{CHF}=\text{CFCF}_2\text{CHF}_2$	1,2,3,3,4,4-hexafluoro-1-butene
	HFC-1336pyy	$\text{CHF}_2\text{CF}=\text{CFCHF}_2$	1,1,2,3,4,4-hexafluoro-2-butene
25	HFC-1336qy	$\text{CH}_2\text{FCF}=\text{CFCF}_3$	1,1,1,2,3,4-hexafluoro-2-butene
	HFC-1336pz	$\text{CHF}_2\text{CH}=\text{CFCF}_3$	1,1,1,2,4,4-hexafluoro-2-butene
	HFC-1336mzy	$\text{CF}_3\text{CH}=\text{CFCHF}_2$	1,1,1,3,4,4-hexafluoro-2-butene
	HFC-1336qc	$\text{CF}_2=\text{CFCF}_2\text{CH}_2\text{F}$	1,1,2,3,3,4-hexafluoro-1-butene
30	HFC-1336pe	$\text{CF}_2=\text{CFCHFCF}_2$	1,1,2,3,4,4-hexafluoro-1-butene
	HFC-1336ft	$\text{CH}_2=\text{C}(\text{CF}_3)_2$	3,3,3-trifluoro-2-(trifluoromethyl)-1-propene
	HFC-1345qz	$\text{CH}_2\text{FCH}=\text{CFCF}_3$	1,1,1,2,4-pentafluoro-2-butene
35	HFC-1345mzy	$\text{CF}_3\text{CH}=\text{CFCH}_2\text{F}$	1,1,1,3,4-pentafluoro-2-butene
	HFC-1345fz	$\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$	3,3,4,4,4-pentafluoro-1-butene
	HFC-1345mzz	$\text{CHF}_2\text{CH}=\text{CHCF}_3$	1,1,1,4,4-pentafluoro-2-butene
	HFC-1345sy	$\text{CH}_3\text{CF}=\text{CFCF}_3$	1,9,1,2,3-pentafluoro-2-butene
40	HFC-1345fyc	$\text{CH}_2=\text{CFCF}_2\text{CHF}_2$	2,3,3,4,4-pentafluoro-1-butene
	HFC-1345pyz	$\text{CHF}_2\text{CF}=\text{CHCHF}_2$	1,1,2,4,4-pentafluoro-2-butene
	HFC-1345cyc	$\text{CH}_3\text{CF}_2\text{CF}=\text{CF}_2$	1,1,2,3,3-pentafluoro-1-butene
45	HFC-1345pyy	$\text{CH}_2\text{FCF}=\text{CFCHF}_2$	1,1,2,3,4-pentafluoro-2-butene
	HFC-1345eyc	$\text{CH}_2\text{FCF}_2\text{CF}=\text{CF}_2$	1,2,3,3,4-pentafluoro-1-butene
	HFC-1345ctm	$\text{CF}_2=\text{C}(\text{CF}_3)(\text{CH}_3)$	1,1,3,3,3-pentafluoro-2-methyl-1-propene
	HFC-1345ftp	$\text{CH}_2=\text{C}(\text{CHF}_2)(\text{CF}_3)$	2-(difluoromethyl)-3,3,3-trifluoro-1-propene
50	HFC1345fye	$\text{CH}_2=\text{CFCHFCF}_3$	2,3,4,4,4-pentafluoro-1-butene
	HFC-1345eyf	$\text{CHF}=\text{CFCH}_2\text{CF}_3$	1,2,4,4,4-pentafluoro-1-butene
	HFC-1345eze	$\text{CHF}=\text{CHCHFCF}_3$	1,3,4,4,4-pentafluoro-1-butene
55	HFC-1345ezc	$\text{CHF}=\text{CHCF}_2\text{CHF}_2$	1,3,3,4,4-pentafluoro-1-butene
	HFC-1345eye	$\text{CHF}=\text{CFCHFCF}_2$	1,2,3,4,4-pentafluoro-1-butene
	HFC-1354fzc	$\text{CH}_2=\text{CHCF}_2\text{CHF}_2$	3,3,4,4-tetrafluoro-1-butene

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(continued)

	Name	Structure	Chemical name
5	HFC-1354ctp	$\text{CF}_2=\text{C}(\text{CHF}_2)(\text{CH}_3)$	1,1,3,3-tetrafluoro-2-methyl-1-propene
	HFC-1354etm	$\text{CHF}=\text{C}(\text{CF}_3)(\text{CH}_3)$	1,3,3,3-tetrafluoro-2-methyl-1-propene
	HFC-1354tfp	$\text{CH}_2=\text{C}(\text{CHF}_2)_2$	2-(difluoromethyl)-3,3-difluoro-1-propene
	HFC-1354my	$\text{CF}_3\text{CF}=\text{CHCH}_3$	1,1,1,2-tetrafluoro-2-butene
10	HFC-1354mzy	$\text{CH}_3\text{CF}=\text{CHCF}_3$	1,1,1,3-tetrafluoro-2-butene
	FC-141-10myy	$\text{CF}_3\text{CF}=\text{CFCF}_2\text{CF}_3$	1,1,1,2,3,4,4,5,5,5-decafluoro-2-pentene
	FC-141-10cy	$\text{CF}_2=\text{CFCF}_2\text{CF}_2\text{CF}_3$	1,1,2,3,3,4,4,5,5,5-decafluoro-1-pentene
15	HFC-1429mzt	$(\text{CF}_3)_2\text{C}=\text{CHCF}_3$	1,1,1,4,4,4-hexafluoro-2-(trifluoromethyl)-2-butene
	HFC-1429myz	$\text{CF}_3\text{CF}=\text{CHCF}_2\text{CF}_3$	1,1,1,2,4,4,5,5,5-nonafluoro-2-pentene
	HFC-1429mzy	$\text{CF}_3\text{CH}=\text{CFCF}_2\text{CF}_3$	1,1,1,3,4,4,5,5,5-nonafluoro-2-pentene
	HFC-1429eyc	$\text{CHF}=\text{CFCF}_2\text{CF}_2\text{CF}_3$	1,2,3,3,4,4,5,5,5-nonafluoro-1-pentene
20	HFC-1429czc	$\text{CF}_2=\text{CHCF}_2\text{CF}_2\text{CF}_3$	1,1,3,3,4,4,5,5,5-nonafluoro-1-pentene
	HFC-1429cycc	$\text{CF}_2=\text{CFCF}_2\text{CF}_2\text{CHF}_2$	1,1,2,3,3,4,4,5,5-nonafluoro-1-pentene
	HFC-1429pyy	$\text{CHF}_2\text{CF}=\text{CFCF}_2\text{CF}_3$	1,1,2,3,4,4,5,5,5-nonafluoro-2-pentene
25	HFC-1429myyc	$\text{CF}_3\text{CF}=\text{CFCF}_2\text{CHF}_2$	1,1,1,2,3,4,4,5,5-nonafluoro-2-pentene
	HFC-1429myye	$\text{CF}_3\text{CF}=\text{CFCHFCF}_3$	1,1,1,2,3,4,5,5,5-nonafluoro-2-pentene
	HFC-1429eyym	$\text{CHF}=\text{CFCF}(\text{CF}_3)_2$	1,2,3,4,4,4-hexafluoro-3-(trifluoromethyl)-1-butene
	HFC-1429cyzm	$\text{CF}_2=\text{CFCH}(\text{CF}_3)_2$	1,1,2,4,4,4-hexafluoro-3-(trifluoromethyl)-1-butene
30	HFC-1429mzt	$\text{CF}_3\text{CH}=\text{C}(\text{CF}_3)_2$	1,1,1,4,4,4-hexafluoro-2-(trifluoromethyl)-2-butene
	HFC-1429czym	$\text{CF}_2=\text{CHCF}(\text{CF}_3)_2$	1,1,3,4,4,4-hexafluoro-3-(trifluoromethyl)-1-butene
	HFC-1438fy	$\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{CF}_3$	2,3,3,4,4,5,5,5-octafluoro-1-pentene
35	HFC-1438eycc	$\text{CHF}=\text{CFCF}_2\text{CF}_2\text{CHF}_2$	1,2,3,3,4,4,5,5,5-octafluoro-1-pentene
	HFC-1438ftmc	$\text{CH}_2=\text{C}(\text{CF}_3)\text{CF}_2\text{CF}_3$	3,3,4,4,4-pentafluoro-2-(trifluoromethyl)-1-butene
	HFC-1438czzm	$\text{CF}_2=\text{CHCH}(\text{CF}_3)_2$	1,1,4,4,4-pentafluoro-3-(trifluoromethyl)-1-butene
	HFC-1438ezym	$\text{CHF}=\text{CHCF}(\text{CF}_3)_2$	1,3,4,4,4-pentafluoro-3-(trifluoromethyl)-1-butene
40	HFC-1438ctmf	$\text{CF}_2=\text{C}(\text{CF}_3)\text{CH}_2\text{CF}_3$	1,1,4,4,4-pentafluoro-2-(trifluoromethyl)-1-butene
	HFC-1447fzy	$(\text{CF}_3)_2\text{CFCH}=\text{CH}_2$	3,4,4,4-tetrafluoro-3-(trifluoromethyl)-1-butene
	HFC-1447fz	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}=\text{CH}_2$	3,3,4,4,5,5,5-heptafluoro-1-pentene
45	HFC-1447fycc	$\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{CHF}_2$	2,3,3,4,4,5,5-heptafluoro-1-pentene
	HFC-1447czcf	$\text{CF}_2=\text{CHCF}_2\text{CH}_2\text{CF}_3$	1,1,3,3,5,5,5-heptafluoro-1-pentene
	HFC-1447mytm	$\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)(\text{CH}_3)$	1,1,1,2,4,4,4-heptafluoro-3-methyl-2-butene
	HFC-1447fyz	$\text{CH}_2=\text{CFCH}(\text{CF}_3)_2$	2,4,4,4-tetrafluoro-3-(trifluoromethyl)-1-butene
50	HFC-1447ezz	$\text{CHF}=\text{CHCH}(\text{CF}_3)_2$	1,4,4,4-tetrafluoro-3-(trifluoromethyl)-1-butene
	HFC-1447qzt	$\text{CH}_2\text{FCH}=\text{C}(\text{CF}_3)_2$	1,4,4,4-tetrafluoro-2-(trifluoromethyl)-2-butene
	HFC-1447syt	$\text{CH}_3\text{CF}=\text{C}(\text{CF}_3)_2$	2,4,4,4-tetrafluoro-2-(trifluoromethyl)-2-butene
55	HFC-1456szt	$(\text{CF}_3)_2\text{C}=\text{CHCH}_3$	3-(trifluoromethyl)-4,4,4-trifluoro-2-butene
	NFC-1456szy	$\text{CF}_3\text{CF}_2\text{CF}=\text{CHCH}_3$	3,4,4,5,5,5-hexafluoro-2-pentene
	HFC-1456mstz	$\text{CF}_3\text{C}(\text{CH}_3)=\text{CHCF}_3$	1,1,1,4,4,4-hexafluoro-2-methyl-2-butene

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	Name	Structure	Chemical name
5	HFC-1456fzce	$\text{CH}_2=\text{CHCF}_2\text{CHFCF}_3$	3,3,4,5,6,5-hexafluoro-1-pentene
	HFC-1456ftmf	$\text{CH}_2=\text{C}(\text{CF}_3)\text{CH}_2\text{CF}_3$	4,4,4-trifluoro-2-(trifluoromethyl)-1-butene
	FC-151-12c	$\text{CF}_5(\text{CF}_2)_3\text{CF}=\text{CF}_2$	1,1,2,3,3,4,4,5,5,6,6,6-dodecafluoro-1-hexene (or perfluoro-1-hexene)
10	FC-151-12mcy	$\text{CF}_3\text{CF}_2\text{CF}=\text{CFCF}_2\text{CF}_3$	1,1,1,2,2,3,4,5,5,6,6,6-dodecafluoro-3-hexene (or perfluoro-3-hexene)
	FC-151-12mmtt	$(\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)_2$	1,1,1,4,4,4-hexafluoro-2,3-bis(trifluoromethyl)-2-butene
	FC-151-12mmzz	$(\text{CF}_3)_2\text{CFCF}=\text{CFCF}_3$	1,1,1,2,3,4,5,5,5-nonafluoro-4-(trifluoromethyl)-2-pentene
15	HFC-152-11mmtz	$(\text{CF}_3)_2\text{C}=\text{CHC}_2\text{F}_5$	1,1,1,4,4,5,5,5-octafluoro-2-(trifluoromethyl)-2-pentene
	HFC-152-11mmyyz	$(\text{CF}_3)_2\text{CFCF}=\text{CHCF}_3$	1,1,1,3,4,5,5,5-octafluoro-4-(trifluoromethyl)-2-pentene
	PFBE (or HFC-1549fz)	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}=\text{CH}_2$	3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene (or perfluorobutylethylene)
20	HFC-1549fztmm	$\text{CH}_2=\text{CHC}(\text{CF}_3)_3$	4,4,4-trifluoro-3,3-bis(trifluoromethyl)-1-butene
	HFC-1549mmmts	$(\text{CF}_3)_2\text{C}=\text{C}(\text{CH}_3)(\text{CF}_3)$	1,1,1,4,4,4-hexafluoro-3-methyl-2-(trifluoromethyl)-2-butene
25	HFC-1549fycz	$\text{CH}_2=\text{CFCF}_2\text{CH}(\text{CF}_3)_2$	2,3,3,5,5,5-hexafluoro-4-(trifluoromethyl)-1-pentene
	HFC-1549myts	$\text{CF}_3\text{CF}=\text{C}(\text{CH}_3)\text{CF}_2\text{CF}_3$	1,1,1,2,4,4,5,5,5-nonafluoro-3-methyl-2-pentene
	HFC-1549mzzz	$\text{CF}_3\text{CH}=\text{CHCH}(\text{CF}_3)_2$	1,1,1,5,5,5-hexafluoro-4-(trifluoromethyl)-2-pentene
	HFC-1558szy	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}=\text{CHCH}_3$	3,4,4,5,5,6,6,6-octafluoro-2-hexene
30	HFC-1558fzccc	$\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$	3,3,4,4,5,5,6,6,6-octafluoro-2-hexene
	HFC-1558mmtzc	$(\text{CF}_3)_2\text{C}=\text{CHCF}_2\text{CH}_3$	1,1,1,4,4-pentafluoro-2-(trifluoromethyl)-2-pentene
	HFC-1558ftmf	$\text{CH}_2=\text{C}(\text{CF}_3)\text{CH}_2\text{C}_2\text{F}_5$	4,4,5,5,5-pentafluoro-2-(trifluoromethyl)-1-pentene
35	HFC-1567fts	$\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{CH}_3)=\text{CH}_2$	3,3,4,4,5,5,5-heptafluoro-2-methyl-1-pentene
	HFC-1567szz	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}=\text{CHCH}_3$	4,4,5,5,6,6,6-heptafluoro-2-hexene
	HFC-1567zfzc	$\text{CH}_2=\text{CHCH}_2\text{CF}_2\text{C}_2\text{F}_5$	4,4,5,5,6,6,6-heptafluoro-1-hexene
	HFC-1567sfyy	$\text{CF}_3\text{CF}_2\text{CF}=\text{CFC}_2\text{H}_5$	1,1,1,2,2,3,4-heptafluoro-3-hexene
40	HFC-1567zfzy	$\text{CH}_2=\text{CHCH}_2\text{CF}(\text{CF}_3)_2$	4,5,5,5-tetrafluoro-4-(trifluoromethyl)-1-pentene
	HFC-1567myzzm	$\text{CF}_3\text{CF}=\text{CHCH}(\text{CF}_3)(\text{CH}_3)$	1,1,1,2,5,5,5-heptafluoro-4-methyl-2-pentene
	HFC-1567mmtyf	$(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{H}_5$	1,1,1,3-tetrafluoro-2-(trifluoromethyl)-2-pentene
45	FC-161-14myy	$\text{CF}_3\text{CF}=\text{CFCF}_2\text{CF}_2\text{C}_2\text{F}_5$	1,1,1,2,3,4,4,5,5,6,6,7,7,7-tetradecafluoro-2-heptene
	FC-161-14mcy	$\text{CF}_3\text{CF}_2\text{CF}=\text{CFCF}_2\text{C}_2\text{F}_5$	1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoro-2-heptene
	HFC-162-13mzy	$\text{CF}_3\text{CH}=\text{CFCF}_2\text{CF}_2\text{C}_2\text{F}_5$	1,1,1,3,4,4,5,5,6,6,7,7,7-tridecafluoro-2-heptene
	HFC-162-13myz	$\text{CF}_3\text{CF}=\text{CHCF}_2\text{CF}_2\text{C}_2\text{F}_5$	1,1,1,2,4,4,5,6,6,6,7,7,7-tridecafluoro-2-heptene
50	HFC-162-13mczy	$\text{CF}_3\text{CF}_2\text{CH}=\text{CFCF}_2\text{C}_2\text{F}_5$	1,1,1,2,2,4,5,5,6,6,7,7,7-tridecafluoro-3-heptene
	HFC-162-13mcyz	$\text{CF}_3\text{CF}_2\text{CF}=\text{CHCF}_2\text{C}_2\text{F}_5$	1,1,1,2,2,3,5,5,6,6,7,7,7-tridecafluoro-3-heptene
	PEVE	$\text{CF}_2=\text{CFOCF}_2\text{CF}_3$	pentafluoroethyl trifluorovinyl ether
55	PMVE	$\text{CF}_2=\text{CFOCF}_3$	trifluoromethyl trifluorovinyl ether

[0036] The compounds listed in Table 2 and Table 3 are available commercially or may be prepared by processes known in the art or as described herein.

[0037] 1,1,1,4,4-pentafluoro-2-butene may be prepared from 1,1,1,2,4,4-hexafluorobutane ($\text{CHF}_2\text{CH}_2\text{CHFCF}_3$) by dehydrofluorination over solid KOH in the vapor phase at room temperature. The synthesis of 1,1,1,2,4,4-hexafluorobutane is described in US 6,066,768. 1,1,1,4,4,4-hexafluoro-2-butene may be prepared from 1,1,1,4,4,4-hexafluoro-2-iodobutane ($\text{CF}_3\text{CHICH}_2\text{CF}_3$) by reaction with KOH using a phase transfer catalyst at about 60°C. The synthesis of 1,1,1,4,4,4-hexafluoro-2-iodobutane may be carried out by reaction of perfluoromethyl iodide (CF_3I) and 3,3,3-trifluoropropene ($\text{CF}_3\text{CH}=\text{CH}_2$) at about 200°C under autogenous pressure for about 8 hours.

[0038] 3,4,4,5,5,5-hexafluoro-2-pentene may be prepared by dehydrofluorination of 1,1,1,2,2,3,3-heptafluoropentane ($\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_3$) using solid KOH or over a carbon catalyst at 200-300 °C. 1,1,1,2,2,3,3-heptafluoropentane may be prepared by hydrogenation of 3,3,4,4,5,5,5-heptafluoro-1-pentene ($\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}=\text{CH}_2$).

[0039] 1,1,1,2,3,4-hexafluoro-2-butene may be prepared by dehydrofluorination of 1,1,1,2,3,3,4-heptafluorobutane ($\text{CH}_2\text{FCF}_2\text{CHFCF}_3$) using solid KOH.

[0040] 1,1,1,2,4,4-hexafluoro-2-butene may be prepared by dehydrofluorination of 1,1,1,2,2,4,4-heptafluorobutane ($\text{CHF}_2\text{CH}_2\text{CF}_2\text{CF}_3$) using solid KOH.

[0041] 1,1,1,3,4,4-hexafluoro-2-butene may be prepared by dehydrofluorination of 1,1,1,3,3,4,4-heptafluorobutane ($\text{CF}_3\text{CH}_2\text{CF}_2\text{CHF}_2$) using solid KOH.

[0042] 1,1,1,2,4-pentafluoro-2-butene may be prepared by dehydrofluorination of 1,1,1,2,2,3-hexafluorobutane ($\text{CH}_2\text{FCH}_2\text{CF}_2\text{CF}_3$) using solid KOH.

[0043] 1,1,1,3,4-pentafluoro-2-butene may be prepared by dehydrofluorination of 1,1,1,3,3,4-hexafluorobutane ($\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_2\text{F}$) using solid KOH.

[0044] 1,1,1,3-tetrafluoro-2-butene may be prepared by reacting 1,1,1,3,3-pentafluorobutane ($\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$) with aqueous KOH at 120 °C.

[0045] 1,1,1,4,4,5,5,5-octafluoro-2-pentene may be prepared from ($\text{CF}_3\text{CHICH}_2\text{CF}_2\text{CF}_3$) by reaction with KOH using a phase transfer catalyst at about 60°C. The synthesis of 4-iodo-1,1,1,2,2,5,5,5-octafluoropentane may be carried out by reaction of perfluoroethyl iodide ($\text{CF}_3\text{CF}_2\text{I}$) and 3,3,3-trifluoropropene at about 200°C under autogenous pressure for about 8 hours.

[0046] 1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene may be prepared from 1,1,1,2,2,5,5,6,6,6-decafluoro-3-iodohexane ($\text{CF}_3\text{CF}_2\text{CHICH}_2\text{CF}_2\text{CF}_3$) by reaction with KOH using a phase transfer catalyst at about 60°C. The synthesis of 1,1,1,2,2,5,5,6,6,6-decafluoro-3-iodohexane may be carried out by reaction of perfluoroethyl iodide ($\text{CF}_3\text{CF}_2\text{I}$) and 3,3,4,4,4-pentafluoro-1-butene ($\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$) at about 200°C under autogenous pressure for about 8 hours.

[0047] 1,1,1,4,5,5,5-heptafluoro-4-(trifluoromethyl)-2-pentene may be prepared by the dehydrofluorination of 1,1,1,2,5,5,5-heptafluoro-4-iodo-2-(trifluoromethyl)-pentane ($\text{CF}_3\text{CHICH}_2\text{CF}(\text{CF}_3)_2$) with KOH in isopropanol. $\text{CF}_3\text{CHICH}_2\text{CF}(\text{CF}_3)_2$ is made from reaction of $(\text{CF}_3)_2\text{CFI}$ with $\text{CF}_3\text{CH}=\text{CH}_2$ at high temperature, such as about 200 °C.

[0048] 1,1,1,4,4,5,5,6,6,6-decafluoro-2-hexene may be prepared by the reaction of 1,1,1,4,4,4-hexafluoro-2-butene ($\text{CF}_3\text{CH}=\text{CHCF}_3$) with tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$) and antimony pentafluoride (SbF_5).

[0049] 2,3,3,4,4-pentafluoro-1-butene may be prepared by dehydrofluorination of 1,1,2,2,3,3-hexafluorobutane over fluorided alumina at elevated temperature.

[0050] 2,3,3,4,4,5,5,5-octafluoro-1-pentene may be prepared by dehydrofluorination of 2,2,3,3,4,4,5,5,5-nonafluoropentane over solid KOH.

[0051] 1,2,3,3,4,4,5,5-octafluoro-1-pentene may be prepared by dehydrofluorination of 2,2,3,3,4,4,5,5,5-nonafluoropentane over fluorided alumina at elevated temperature.

[0052] Many of the compounds of Formula I, Formula II, Table 1, Table 2 and Table 3 exist as different configurational isomers or stereoisomers. When the specific isomer is not designated, the present invention is intended to include all single configurational isomers, single stereoisomers, or any combination thereof. For instance, F11 E is meant to represent the *E*-isomer, *Z*-isomer, or any combination or mixture of both isomers in any ratio. As another example, HFC-1225ye is meant to represent the *E*-isomer, *Z*-isomer, or any combination or mixture of both isomers in any ratio.

[0053] In one embodiment, the present invention provides a composition comprising at least one fluoroolefin and a stabilizer comprising an effective amount of a terephthalate selected from divinyl terephthalate (CAS reg. no. [13486-19-0]) and diphenyl terephthalate (CAS reg. no. [1539-04-4]), and mixtures of the foregoing terephthalates.

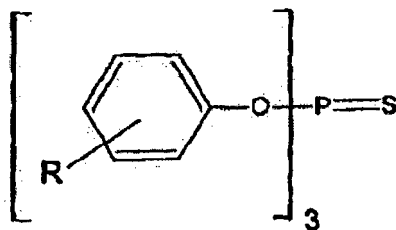
[0054] In another embodiment, the stabilizer may additionally comprise nitromethane (CH_3NO_2 , CAS reg. no. [75-52-5]) and/or ascorbic acid (CAS reg. no. [50-81-7]).

[0055] In another embodiment, the stabilizer comprising at least one terephthalate selected from divinyl terephthalate and diphenyl terephthalate is combined with at least one additional stabilizer comprising at least one compound selected from the group consisting of phenols, thiophosphates, butylated triphenylphosphorothionates, organo phosphates, phosphites, terpenes, terpenoids, fullerenes, aryl alkyl ethers, functionalized perfluoropolyethers, polyoxyalkylated aromatics, alkylated aromatics, epoxides, fluorinated epoxides, oxetanes, thiols, thioethers, amines, alkylsilanes, benzophenone derivatives, aryl sulfides, and mixtures thereof.

[0056] In one embodiment, the additional stabilizers comprise at least one thiophosphate. The thiophosphate stabilizers of the present invention are compounds derived from phosphoric acids by substituting divalent sulfur for one or more

oxygen atoms. These may be monothiophosphates, dithiophosphates or higher order thiophosphates. A representative dithiophosphate is commercially available from Ciba Specialty Chemicals of Basel, Switzerland (hereinafter "Ciba") under the trademark Irgalube® 63. In another embodiment, thiophosphates include dialkylthiophosphate esters. A representative dialkylthiophosphate ester stabilizer is commercially available from Ciba under the trademark Irgalube® 353.

[0057] In one embodiment, the additional stabilizers comprise at least one butylated triphenylphosphorothionate. The butylated triphenylphosphorothionate stabilizers of the present invention are as depicted by Formula A.



Formula A

An example of a butylated triphenylphosphorothionate, wherein each R is independently selected from H or tert-butyl, is commercially available from Ciba under the trademark Irgalube® 232.

[0058] In one embodiment, the additional stabilizers comprise at least one organophosphate. The organophosphate stabilizers suitable for use as a stabilizer according to the present invention include but are not limited to amine phosphates, trialkyl phosphates, triaryl phosphates, mixed alkyl-aryl phosphates (alkyldiaryl, dialkylaryl or alkylated aryl), alkylated triaryl phosphates, and cyclic phosphates, and mixtures thereof. A representative amine phosphate is commercially available from Ciba under the trademark Irgalube® 349. Representative trialkyl phosphates include: trimethyl phosphate ((CH₃)₃PO₄, Cas reg. no. 512-56-1); triethyl phosphate ((CH₃CH₂)₃PO₄, Cas reg. no. 78-40-0); tributyl phosphate ((C₄H₉)₃PO₄, CAS reg. no. 126-73-8); trioctyl phosphate ((C₈H₁₇)₃PO₄, CAS reg. no. 1806-54-8); and tri(2-ethylhexyl)phosphate ((CH₃CH(C₂H₅)(CH₂)₄)₃PO₄, CAS reg. no. 78-42-2). Representative triaryl phosphates include: triphenyl phosphate ((C₆H₅O)₃PO, CAS reg. no. 115-86-6); tricresyl phosphate (TCP, (CH₃C₆H₄O)₃PO, CAS reg. no. 1330-78-5); and trixylenyl phosphate (((CH₂)₂C₆H₃O)₃PO, CAS reg. no. 25155-23-1). Representative mixed alkyl-aryl phosphates include: isopropylphenyl phenyl phosphate (IPPP, (C₆H₅O)₂((CH₃)₂CHO)PO, CAS reg. no. 68782-95-6) and bis(t-butylphenyl) phenyl phosphate (TBPP, (C₆H₅O)₂((CH₃)₃C)PO, CAS reg. no. 65652-41-7). Such phosphorus compounds. All of the organophosphate stabilizers listed in this paragraph are available from multiple chemical suppliers such as Aldrich (Milwaukee, Wisconsin); Alfa Aesar (Ward Hill, MA); or Akzo Nobel (Arnhem, the Netherlands). The alkylated triaryl phosphates include butylated triphenyl phosphates, tert-butylated triphenyl phosphate, iso-propylated triphenyl phosphates. Representative commercially available alkylated triaryl phosphates include a butylated triphenyl phosphate, commercially available from Akzo Nobel (Arnhem, the Netherlands) under the trademark Syn-O-Ad® 8784; a tert-butylated triphenyl phosphate commercially available from Great Lakes Chemical Corporation (GLCC, West Lafayette, IN) under the trademark Durad® 620; and iso-propylated triphenyl phosphates, also commercially available from GLCC under the trademarks Durad® 220 and 110.

[0059] In another embodiment, the additional stabilizer may comprise at least one phosphite. Phosphite stabilizers may be derived from substituted phosphites, including hindered phosphites. In particular, hindered phosphites are derivatives of alkyl, aryl or alkylaryl phosphite compounds. The hindered phosphites include tris-(di-tert-butylphenyl) phosphite, di-n-octyl phosphite, and iso-decyl diphenyl phosphate. Tris-(di-tert-butylphenyl) phosphite is sold under the trademark Irgafos® 168, di-n-octyl phosphite is sold under the trademark Irgafos® OPH, and iso-decyl diphenyl phosphite) is sold under the trademark Irgafos® DDPP, all by Ciba.

[0060] In another embodiment, the additional stabilizer may comprise at least one phenol. Phenol stabilizers comprise any substituted or unsubstituted phenol compound including phenols comprising one or more substituted or unsubstituted cyclic, straight chain, or branched aliphatic substituent group, such as, alkylated monophenols including 2,6-di-tert-butyl-4-methylphenol; 2,6-di-tert-butyl-4-ethylphenol; 2,4-dimethyl-6-tertbutylphenol; tocopherol; and the like, hydroquinone and alkylated hydroquinones including t-butyl hydroquinone, other derivatives of hydroquinone; and the like, hydroxylated thiodiphenyl ethers, including 4,4'-thio-bis(2-methyl-6-tert-butylphenol); 4,4'-thiobis(3-methyl-6-tertbutylphenol); 2,2'-thiobis(4-methyl-6-tert-butylphenol); and the like, alkylidene-bisphenols including, 4,4'-methylenebis(2,6-di-tert-butylphenol); 4,4'-bis(2,6-di-tert-butylphenol); derivatives of 2,2'- or 4,4'-biphenoldiols; 2,2'-methylenebis(4-ethyl-6-tertbutylphenol); 2,2'-methylenebis(4-methyl-6-tertbutylphenol); 4,4'-butylidenebis(3-methyl-6-tert-butylphenol); 4,4'-isopropylidenebis(2,6-di-tert-butylphenol); 2,2'-methylenebis(4-methyl-6-nonylphenol); 2,2'-isobutylidenebis(4,6-dimethylphenol); 2,2'-methylenebis(4-methyl-6-cyclohexylphenol, 2,2'- or 4,4'- biphenyldiols including 2,2'-methylenebis(4-ethyl-6-tert-butylphenol); butylatedhydroxy toluene (BHT), bisphenols comprising heteroatoms including 2,6-di-tert-alpha-dimethyl-

amino-p-cresol, 4,4-thiobis(6-tert-butyl-m-cresol); and the like; acylaminophenols; 2,6-di-tert-butyl-4(N,N'-dimethylaminomethylphenol); sulfides including; bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulfide; bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide; and mixtures thereof, meaning mixtures of any of the phenol stabilizers listed in this paragraph.

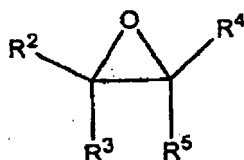
[0061] In another embodiment, the additional stabilizer may comprise at least one terpene. Terpenes comprise hydrocarbon compounds characterized by structures containing more than one repeating isoprene (2-methyl-1,3-butadiene) unit. Representative terpenes include but are not limited to myrcene (2-methyl-6-methyl-eneocta-1,7-diene), allo-ocimene, beta-ocimene, terebene, limonene (in particular d-limonene), retinal, pinene, menthol, geraniol, farnesol, phytol, Vitamin A, terpinene, delta-3-carene, terpinolene, phellandrene, fenchene, dipentene, and mixtures thereof, meaning mixtures of any of the terpene stabilizers listed in this paragraph. Terpene stabilizers are commercially available or may be prepared by methods known in the art or isolated from natural sources.

[0062] In another embodiment, the additional stabilizer may comprise at least one terpenoid. Terpenoids comprise natural products and related compounds characterized by structures containing more than one repeating isoprene unit and usually contain oxygen. Representative terpenoids include carotenoids, such as lycopene (CAS reg. no. [502-65-8]), beta carotene (CAS reg. no. [7235-40-7]), and xanthophylls, i.e. zeaxanthin (CAS reg. no. [144-68-3]); retinoids, such as hepaxanthin (CAS reg. no. [512-39-0]), and isotretinoin (CAS reg. no. [4759-48-2]); abietane (CAS reg. no. [640-43-7]); ambrosane (CAS reg. no. [24749-18-6]); aristolane (CAS reg. no. [29786-49-6]); atisane (CAS reg. no. [24379-83-7]); beyerane (CAS reg. no. [2359-83-3]); bisabolane (CAS reg. no. [29799-19-7]); bornane (CAS reg. no. [464-15-3]); caryophyllane (CAS reg. no. [20479-00-9]); cedrane (CAS reg. no. [13567-54-9]); dammarane (CAS reg. no. [545-22-2]); drimane (CAS reg. no. [5951-58-6]); eremophilane (CAS reg. no. [3242-05-5]); eudesmane (CAS reg. no. [473-11-0]); fenchane (CAS reg. no. [6248-88-0]); gammacerane (CAS reg. no. [559-65-9]); germacrane (CAS reg. no. [645-10-3]); gibbane (CAS reg. no. [6902-95-0]); grayanotoxane (CAS reg. no. [39907-73-8]); guaiane (CAS reg. no. [489-80-5]); himachalane (CAS reg. no. [20479-45-2]); hopane (CAS reg. no. [471-62-5]); humulane (CAS reg. no. [430-19-3]); kaurane (CAS reg. no. [1573-40-6]); labdane (CAS reg. no. [561-90-0]); lanostane (CAS reg. no. [474-20-4]); lupane (CAS reg. no. [464-99-3]); p-menthane (CAS reg. no. [99-82-1]); oleanane (CAS reg. no. [471-67-0]); ophiobolane (CAS reg. no. [20098-65-1]); picrasane (CAS reg. no. [35732-97-9]); pimarane (CAS reg. no. [30257-03-5]); pinane (CAS reg. no. [473-55-2]); podocarpane (CAS reg. no. [411-78-3]); protostane (CAS reg. no. [70050-78-1]); rosane (CAS reg. no. [6812-82-4]); taxane (CAS reg. no. [1605-68-1]); thujane (CAS reg. no. [471-12-5]); trichothecane (CAS reg. no. [24706-08-9]), ursane (CAS reg. no. [464-93-7]), and mixtures thereof, meaning mixtures of any of the terpenoids listed in this paragraphs. The terpenoids of the present invention are commercially available or may be prepared by methods known in the art or may be isolated from the naturally occurring source.

[0063] In another embodiment, the additional stabilizer may comprise at least one fullerene. Fullerenes comprise closed carbon cages that are bonded as hexagonal carbon rings (benzene) linked to each other partly via pentagons. The relationship between the number of apices (a, carbon atoms) and hexagon carbon rings (n) (pentagon rings always number 12) is given by: $a = 2(n+10)$. While this formula provides for all theoretical structures, only those molecules with relatively low stress and distortion will be stable. Representative fullerenes include but are not limited to Buckminsterfullerene (C₆₀, or "bucky ball", CAS reg. no. [99685-96-8]), and [5,6]fullerene-C₇₀ (C₇₀, CAS reg. no. [115383-22-7]), fullerene-C₇₆ (CAS reg. no. [135113-15-4]), fullerene-C₇₈ (CAS reg. no. [136316-32-0]), and fullerene-C₈₄ (CAS reg. no. [135113-16-5]), and mixtures thereof, meaning mixtures of any of the fullerene stabilizers listed in this paragraph. Fullerenes are commercially available.

[0064] In another embodiment, the additional stabilizer may comprise at least one epoxide. Epoxides comprise at least one compound selected from the group consisting of 1,2-propylene oxide (CAS reg. no. [75-56-9]), 1,2-butylene oxide (CAS reg. no. [106-88-7]), butylphenylglycidyl ether, pentylphenylglycidyl ether, hexylphenylglycidyl ether, heptylphenylglycidyl ether, octylphenylglycidyl ether, nonylphenylglycidyl ether, decylphenylglycidyl ether, glycidyl methylphenylether, 1,4-glycidyl phenyl diether, 4-methoxyphenylglycidyl ether, naphthyl glycidyl ether, 1,4-diglycidyl naphthyl diether, butylphenyl glycidyl ether, n-butyl glycidyl ether, isobutyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, polypropylene glycol diglycidyl ether, and mixtures thereof, meaning mixtures of any of the foregoing epoxides listed in this paragraph.

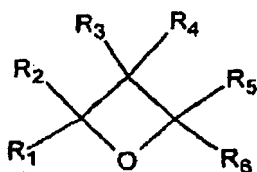
[0065] In another embodiment, the additional stabilizer may comprise at least one fluorinated epoxide. The fluorinated epoxides comprise compounds as depicted by Formula B, wherein each of R² through R⁵ is H, alkyl of 1 to 6 carbon atoms or fluoroalkyl of 1 to 6 carbon atoms with the proviso that at least one of R² through R⁵ is a fluoroalkyl group.



Formula B

Representative fluorinated epoxide stabilizers include but are not limited to trifluoromethyloxirane and 1,1-bis(trifluoromethyl)oxirane, and mixtures thereof, meaning mixtures of any of the foregoing fluorinated epoxide stabilizers. Such compounds may be prepared by methods known in the art, for instance by methods described in, Journal of Fluorine Chemistry, volume 24, pages 93-104 (1984), Journal of Organic Chemistry, volume 56, pages 3187 to 3189 (1991), and Journal of Fluorine Chemistry, volume 125, pages 99-105 (2004).

[0066] In another embodiment, the additional stabilizer may comprise at least one oxetane. The oxetane stabilizers comprise compounds with one or more oxetane groups. These compounds are represented by Formula C, wherein R_1 - R_6 are the same or different and can be selected from hydrogen, alkyl or substituted alkyl, aryl or substituted aryl.



Formula C

Representative oxetane stabilizers include but are not limited to 3-ethyl-3-hydroxymethyl-oxetane, such as OXT-101 (Toagosei Co., Ltd); 3-ethyl-3-((phenoxy)methyl)-oxetane, such as OXT-211 (Toagosei Co., Ltd); and 3-ethyl-3-((2-ethyl-hexyloxy)methyl)-oxetane, such as OXT-212 (Toagosei Co., Ltd), and mixtures thereof, meaning mixtures of any of the oxetanes listed in this paragraph.

[0067] In another embodiment, the additional stabilizer may comprise at least one thiol. The thiol compounds, also known as mercaptans or hydrosulfides, comprise sulfur analogs of the hydroxyl group containing alcohols. Representative thiol stabilizers include but are not limited to methanethiol (methyl mercaptan), ethanethiol (ethyl mercaptan), Coenzyme A (CAS reg. no. [85-61-0]), dimercaptosuccinic acid (DMSA, CAS reg. no. [2418-14-6]), grapefruit mercaptan ((R)-2-(4-methylcyclohex-3-enyl)propane-2-thiol, CAS reg. no. [83150-78-1]), cysteine ((R)-2-amino-3-sulfanyloxypropanoic acid, CAS reg. no. [52-90-4]), and lipoamide (1,2-dithiolane-3-pentanamide, CAS reg. no. [940-69-2]), and mixtures thereof, meaning mixtures of any of the thiols listed in this paragraph.

[0068] In another embodiment, the additional stabilizer may comprise at least one thioether. Thioethers include but are not limited to benzyl phenyl sulfide (CAS reg. no. [831-91-4]), diphenyl sulfide (CAS reg. no. [139-66-2]), dibenzyl sulfide, dioctadecyl 3,3'-thiodipropionate, commercially available from Ciba under the trademark Irganox® PS 802 (Ciba) and didodecyl 3,3'-thiodipropionate, commercially available from Ciba under the trademark Irganox® PS 800 (Ciba), and mixtures thereof, meaning mixtures of any of the thioethers listed in this paragraph.

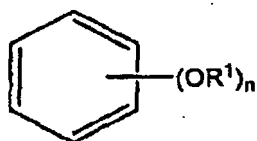
[0069] In another embodiment, the additional stabilizer may comprise at least one amine. In one embodiment, amines comprise at least one compound selected from the group consisting of triethylamine, tributylamine, diisopropylamine, triisopropylamine, triisobutylamine, p-phenylenediamine, and diphenylamine. In another embodiment, the amine stabilizers comprise dialkylamines including (N-(1-methylethyl)-2-propylamine, CAS reg. no. [108-18-9]). In another embodiment, the amine stabilizers include hindered amine antioxidants. Hindered amine antioxidants include amines derived from substituted piperidine compounds, in particular derivatives of an alkyl-substituted piperidyl, piperidinyl, piperazinone, or alkoxy-piperidinyl compounds. Representative hindered amine antioxidants include 2,2,6,6-tetramethyl-4-piperidone; 2,2,6,6-tetramethyl-4-piperidinol; bis-(1,2,2,6,6-pentamethylpiperidyl)sebacate (CAS reg. no. [41556-26-7]); di-(2,2,6,6-tetramethyl-4-piperidyl)sebacate, such as the hindered amine commercially available under the trademark Tinuvin® 770 by Ciba; poly-(N-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate (CAS reg. no. [65447-77-0]), such as that commercially available under the trademark Tinuvin® 622LD from Ciba; alkylated paraphenylenediamines, such as N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine, or N,N'-di-sec-butyl-p-phenylenediamine; and hydroxylamines such as tallow amines or N-methylbis(hydrogenated tallow alkyl)amine. Some other hindered amine antioxidants include

the amine antioxidant commercially available from Ciba under the trademark Tinuvin® 765, or commercially available from Mayzo, Inc. under the trademark BLS® 1944 and BLS® 1770. The amines also include mixtures of any of the amines listed in this paragraph.

[0070] In another embodiment, the additional stabilizer may comprise at least one alkylsilane. Alkylsilanes include but are not limited to bis(dimethylamino)methylsilane (DMAMS, CAS reg. no. [22705-33-5]), tris(trimethylsilyl)silane (TMSS, CAS reg. no. [1873-77-4]), vinyltriethoxysilane (VTES, CAS reg. no. [78-08-0]), and vinyltrimethoxysilane (VTMO, CAS reg. no. [2768-02-7]), and mixtures thereof, meaning mixtures of any of the alkylsilanes listed in this paragraph.

[0071] In another embodiment, the additional stabilizer may comprise at least one aryl sulfide. The aryl sulfides comprise at least one selected from the group consisting of benzyl phenyl sulfide, diphenyl sulfide, and dibenzyl sulfide, and mixtures of any of the foregoing aryl sulfides.

[0072] In one embodiment, the stabilizer may comprise at least one aryl alkyl ether. The aryl alkyl ether stabilizers comprise compounds as depicted by Formula D, wherein n is 1, 2 or 3 and R¹ is an alkyl group of 1 to 16 carbon atoms.



Formula D

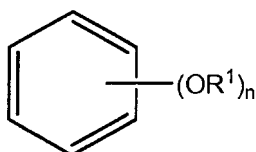
Representative aryl alkyl ethers include but are not limited to anisole, 1,4-dimethoxybenzene, 1,4-diethoxybenzene and 1,3,5-trimethoxybenzene, and mixtures thereof, meaning mixtures of any of the aryl alkyl ethers listed in the paragraph.

[0073] In another embodiment, the stabilizer may comprise at least one polyoxyalkylated aromatic. The polyoxyalkylated aromatics comprise compounds represented by Formula D wherein the R¹ group is a polyoxyalkylated group comprising at least one -CH₂CH₂O- moiety.

[0074] In another embodiment, the stabilizer may comprise at least one alkylated aromatic. Representative alkylated aromatics which can be used as additional stabilizers according to the present invention include but are not limited to alkylbenzene lubricants, both branched and linear, commercially available under the trademarks Zerol® 75, Zerol® 150 and Zerol® (linear alkylbenzenes) 500 from Shrieve Chemicals and HAB 22 (branched alkylbenzene) sold by Nippon Oil.

[0075] In one embodiment, the additional stabilizer comprises at least one functionalized perfluoropolyether. In particular, functionalized-perfluoropolyethers comprise perfluoropolyether- or perfluoroalkyl-containing and phosphorus-containing partially esterified aryl phosphates, aryl phosphonates and salts thereof, containing either (i) a mono- or poly-alkylene oxide linking group between the phosphorus and a fluorocarbon group, or (ii) no linking group between the phosphorus and fluorocarbon group as described in U. S. Patent No. 6,184,187, and references therein.

[0076] In another embodiment, the functionalized perfluoropolyether stabilizers may be compounds as represented by Formula D,

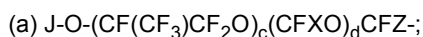


Formula D

which contain either a perfluoroalkyl or perfluoropolyether side chain.

[0077] In another embodiment, the functionalized perfluoropolyether stabilizers may be perfluoropolyether alkyl alcohols comprising a perfluoropolyether segment and one or more alcohols segments having a general formula, -CH₂(C_qH_{2q})OH, wherein -C_qH_{2q} represents a divalent linear or branched alkyl radical where q is an integer from 1 to about 10 as described in U. S. Patent Application Publication No. 2006/0287559.

[0078] In another embodiment, the functionalized perfluoropolyether stabilizers of the present invention may comprise substituted aryl pnictogen compositions having the structure [R_f¹-(C_tR_(u+v))]_mE(O)_n(C_tR₁^(u+v+1))_(3-m), wherein R_f¹ is a fluoropolyether chain having a formula weight ranging from about 400 to about 15,000, comprises repeat units, and is selected from the group consisting of:



- (b) $J^1\text{-O-(CF}_2\text{CF}_2\text{O)}_e(\text{CF}_2\text{O)}_f\text{CFZ}^1\text{-}$;
 (c) $J^2\text{-O-(CF(CF}_3\text{)CF}_2\text{O)}_j\text{CF(CF}_3\text{)CF}_2\text{-}$;
 (d) $J^3\text{-O-(CQ}_2\text{-CF}_2\text{CF}_2\text{-O)}_k\text{-CQ}_2\text{-CF}_2\text{-}$;
 (e) $J^3\text{-O-(CF(CF}_3\text{)CF}_2\text{O)}_g(\text{CF}_2\text{CF}_2\text{O)}_h(\text{CFXO)}_i\text{-CFZ-}$;
 (f) $J^4\text{-O-(CF}_2\text{CF}_2\text{O)}_r\text{CF}_2\text{-}$; and
 (h) combinations of two or more thereof, wherein:

J is a fluoroalkyl group selected from the group consisting of CF_3 , C_2F_5 , C_3F_7 , CF_2Cl , $\text{C}_2\text{F}_4\text{Cl}$, $\text{C}_3\text{F}_6\text{Cl}$, and combinations of two or more thereof;

c and d are numbers such that the ratio of c:d ranges from about 0.01 to about 0.5;

X is F, CF_3 , or combinations thereof;

Z is F, Cl or CF_3 ;

J^1 is a fluoroalkyl group selected from the group consisting of CF_3 , C_2F_5 , C_3F_7 , CF_2Cl , $\text{C}_2\text{F}_4\text{Cl}$, and combinations of two or more thereof;

e and f are numbers such that the ratio of e:f ranges from about 0.3 to about 5;

Z^1 is F or Cl;

J^2 is C_2F_5 , C_3F_7 , or combinations thereof;

j is an average number such that the formula weight of R_f ranges from about 400 to about 15,000;

J^3 is selected from the group consisting of CF_3 , C_2F_5 , C_3F_7 , and combinations of two or more thereof;

k is an average number such that the formula weight of R_f ranges from about 400 to about 15,000;

each Q is independently F, Cl, or H;

g, h and i are numbers such that (g + h) ranges from about 1 to about 50, the ratio of i:(g + h) ranges from about 0.1 to about 0.5;

J^4 is CF_3 , C_2F_5 , or combinations thereof;

r is an average number such that the formula weight of R_f ranges from about 400 to about 15,000; and

each R and R^1 is independently H, a $\text{C}_1\text{-C}_{10}$ alkyl, a halogen, OR^3 , OH, SO_3M , NR^2_2 , R^3OH , $\text{R}^3\text{SO}_3\text{M}$, R^3NR^2_2 , R^3NO_2 , R^3CN , C(O)OR^3 , C(O)OM , C(O)R^3 , or C(O)NR^2_2 , or combinations of two or more thereof; wherein

R^2 is independently H, $\text{C}_1\text{-C}_{10}$ alkyl, or combinations of two or more thereof;

R^3 is a $\text{C}_1\text{-C}_{10}$ alkyl; and

M is hydrogen or a metal, preferably not aluminum;

t is equal to (6+u);

u is any combination of 0, 2, 4, 6, 8, 10, 12, 14, 16;

v is independently either 2 or 4;

n is 0 or 1;

E is P, As, or Sb; and

m is greater than about 0.5 to about 3, provided that, when $\text{E} = \text{P}$, $m = 3.0$ and $t = 6$, R cannot be exclusively H or contain F; as described in U. S. Patent Application Publication No. 2006/0293195.

[0079] In another embodiment, the functionalized perfluoropolyether stabilizers of the present invention may comprise aryl perfluoropolyethers, which are monofunctional aryl perfluoropolyethers having the formula of $\text{R}_f(\text{Y})_a\text{-(C}_t\text{R}_{(u+v)})\text{-(O-C}_t\text{R}^1_{(u+v)})_b\text{-R}_1$ difunctional aryl perfluoropolyethers having the formula of $\text{R}_f^1\text{-[(Y)}_a\text{-(C}_t\text{R}_{(u+v)})\text{-(O-C}_t\text{R}^1_{(u+v)})_b\text{-R]}_2$, or combinations thereof, wherein:

each of R_f and R_f^1 has a formula weight of about 400 to about 15,000;

R_f comprises repeat units selected from the group consisting of

- (a) $\text{J-O-(CF(CF}_3\text{)CF}_2\text{O)}_c(\text{CFXO)}_d\text{CFZ-}$,
 (b) $\text{J}^1\text{-O-(CF}_2\text{CF}_2\text{O)}_e(\text{CF}_2\text{O)}_f\text{CFZ}^1\text{-}$,
 (c) $\text{J}^2\text{-O-(CF(CF}_3\text{)CF}_2\text{O)}_j\text{CF(CF}_3\text{)-}$,
 (d) $\text{J}^3\text{-O-(CQ}_2\text{-CF}_2\text{CF}_2\text{-O)}_k\text{-CQ}_2\text{-}$,
 (e) $\text{J}^3\text{-O-(CF(CF}_3\text{)CF}_2\text{O)}_g(\text{CF}_2\text{CF}_2\text{O)}_h(\text{CFX-O)}_i\text{-CFZ-}$,
 (f) $\text{J}^4\text{-O-(CF}_2\text{CF}_2\text{O)}_r\text{CF}_2\text{-}$, and
 (g) combinations of two or more thereof; and

where

the units with formulae $\text{CF}_2\text{CF}_2\text{O}$ and CF_2O are randomly distributed along the chain;

J is CF₃, C₂F₅, C₃F₇, CF₂Cl, C₂F₄Cl, C₃F₆Cl, or combinations of two or more thereof;

c and d are numbers such that the c/d ratio ranges from about 0.01 to about 0.5;

X is -F, -CF₃, or combinations thereof;

Z is -F, -Cl or -CF₃;

Z¹ is -F or -Cl,

J¹ is CF₃, C₂F₅, C₃F₇, CF₂Cl, C₂F₄Cl, or combinations of two or more thereof;

e and f are numbers such that the e/f ratio ranges from about 0.3 to about 5;

J² is -C₂F₅, -C₃F₇, or combinations thereof;

j is an average number such that the formula weight of R_f ranges from about 400 to about 15,000;

J³ is CF₃, C₂F₅, C₃F₇, or combinations of two or more thereof;

k is an average number such that the formula weight of R_f ranges from about 400 to about 15,000;

each Q is independently -F, -Cl, or -H;

g, h and i are numbers such that (g + h) ranges from about 1 to about 50, the i/(g + h) ratio ranges from about 0.1 to about 0.5;

J⁴ is CF₃, C₂F₅, or combinations thereof;

k' is an average number such that the formula weight of R_f ranges from about 400 to about 15,000;

each R is independently -H, a halogen, -OH, -SO₃M, NR³₂, -NO₂, -R⁴OH, -R⁴SO₃M, -R⁴NR³₂, -R⁴NO₂, -R⁴CN, -C(O)OR⁴, -C(O)OM, -C(O)R⁴, -C(O)NR³₂, or combinations of two or more thereof, except that when b = 0, R cannot

be four hydrogen atoms and -OH, or -Br, or -NH₂; or R cannot be solely H or -NO₂, or combinations thereof;

each R¹ is independently H, -R⁴, -OR⁴, a halogen, -OH, -SO₃M, -NR³₂, -NO₂, -CN, -R⁴OH, -R⁴SO₃M, -R⁴NR³₂, -R⁴NO₂, -R⁴CN, -C(O)OR⁴, -C(O)OM, -C(O)R⁴, C(O)NR³₂, or combinations of two or more thereof provided that if b = 0, the combination of R and R² cannot be four or more hydrogen atoms and -OH, -Br, -NH₂, or -NO₂;

each R³ is independently H, C₁-C₁₀ alkyl, or combinations of two or more thereof;

R⁴ is a C₁-C₁₀ alkyl;

M is a hydrogen or metal ion;

a is 0 or 1;

b is 0-5;

Y is a divalent radical -CH₂OCH₂-, -(CH₂)_o-O-, -(CF₂)_n-, -CF₂O-, -CF₂OCF₂-, -C(O)-, -C(S)-, or combinations of two or more thereof;

n is about 1 to about 5;

o is about 2 to about 5;

t is equal to 6+u;

u is any combination of 0, 2, 4, 6, 8, 10, 12, 14, 16;

v is independently either 2 or 4;

Rf¹ is -(CF₂CF₂O)_e(CF₂O)_fCF₂-, -(C₃F₆O)_p(CF₂CF₂O)_q(CFXO)_rCF₂-,
-(CF₂CF₂O)(C₃F₆O)_wCF(CF₃)-, -CF(CF₃)O(C₃F₆O)_w-Rf²-O(C₃F₆O)_wCF(CF₃)-,
-((CQ₂)CF₂CF₂O)_sCF₂CF₂-, or combinations of two or more thereof;

where

e, f, X, and Q are as defined above;

p, q and r are numbers such that (p+q) ranges from 1 to 50 and r/(p+q) ranges from 0.1 to 0.05;

each w is independently 2 to 45;

Rf² is linear or branched -C_mF_{2m}-;

m is 1-10; and

s is an average number such that the formula weight of R_f¹ ranges from 400 to 15,000, as described in U.S. Patent Application Publication No. 2007/0049502.

[0080] In another embodiment, the additional stabilizer may comprise at least one lactone. Lactones comprise cyclic esters that may be produced by the reaction of an alcohol group with a carboxylic acid group in the same molecule. Representative lactone stabilizers of the present invention include but are not limited to gamma-butyrolactone (CAS reg. no. [96-48-0]), delta-gluconolactone (CAS reg. no. [90-80-2]), gamma-undecalactone (CAS reg. no. [104-67-6]), 6,7-dihydro-4(5H)-benzofuranone (CAS reg. No. [16806-93-2]), and 5,7-bis(1,1-dimethylethyl)-3-[2,3(or 3,4)-dimethylphe-

nyl]-2(3H)-benzofuranone (CAS reg. no. [201815-03-4]), commercially available from Ciba under the trademark Irganox® HP-136, and mixtures thereof, meaning mixtures of any of the lactones listed in this paragraph.

[0081] In another embodiment, the additional stabilizer comprises at least one benzophenone derivative. Benzophenone derivatives comprise benzophenone that may be substituted with side groups including halides, such as fluorine, chlorine, bromine or iodine, amino groups, hydroxyl groups, alkyl groups such as methyl, ethyl or propyl groups, aryl groups such as phenyl, nitro groups, or any combinations of such groups. Representative benzophenone derivative stabilizers include but are not limited to: 2,5-difluorobenzophenone; 2',5'-dihydroxyacetophenone; 2-aminobenzophenone; 2-chlorobenzophenone; 2-fluorobenzophenone; 2-hydroxybenzophenone; 2-methylbenzophenone; 2-amino-4'-chlorobenzophenone; 2-amino-4'-fluorobenzophenone; 2-amino-5-bromo-2'-chlorobenzophenone; 2-amino-5-chlorobenzophenone; 2-amino-5-chloro-2'-fluorobenzophenone; 2-amino-5-nitrobenzophenone; 2-amino-5-nitro-2'-chlorobenzophenone; 2-amino-2',5-dichlorobenzophenone; 2-chloro-4'-fluorobenzophenone; 2-hydroxy-4-methoxybenzophenone; 2-hydroxy-5-chlorobenzophenone; 2-methylamino-5-chlorobenzophenone; 3-methylbenzophenone; 3-nitrobenzophenone; 3-nitro-4'-chloro-4'-fluorobenzophenone; 4-chlorobenzophenone; 4-fluorobenzophenone; 4-hydroxybenzophenone; 4-methoxybenzophenone; 4-methylbenzophenone; 4-nitrobenzophenone; 4-phenylbenzophenone; 4-chloro-3-nitrobenzophenone; 4-hydroxy-4'-chlorobenzophenone; 2,4-dihydroxybenzophenone; 2,4-dimethylbenzophenone; 2,5-dimethylbenzophenone; 3,4-diaminobenzophenone; 3,4-dichlorobenzophenone; 3,4-difluorobenzophenone; 3,4-dihydroxybenzophenone; 3,4-dimethylbenzophenone; 4,4'-bis(diethylamine)benzophenone; 4,4'-bis(dimethylamine)benzophenone; 4,4'-dichlorobenzophenone; 4,4'-difluorobenzophenone; 4,4'-dihydroxybenzophenone; and 4,4'-dimethoxybenzophenone, and mixtures thereof, meaning mixtures of any of the benzophenone derivatives listed in this paragraph.

[0082] In another embodiment, the additional stabilizers comprise at least one alkylsilane. A silane is any silicon analogue of an alkane hydrocarbon. Silanes consist of a chain of silicon atoms covalently bound to hydrogen atoms. An alkyl silane stabilizer of the present invention comprises a substituted silane represented by the general formula $\text{Si}_n\text{R}_{2n+2}$, wherein each R may independently be H; an additional silyl group; an alkyl group, including CH_3 , C_2H_5 , C_3H_7 (any isomer), C_4F_9 (any isomer), and the like; an alkoxy group including methoxy, ethoxy, and the like; an amine group; a vinyl group; or a phenyl group. The R groups may also be substituted with halogens, including Cl, F, and the like or amine groups. Alkylsilanes include but are not limited to bis(dimethylamino)methylsilane (DMAMS, CAS reg. no. [22705-33-5]), tris(trimethylsilyl)silane (TTMSS, CAS reg. no. [1873-77-4]), vinyltriethoxysilane (VTES, CAS reg. no. [78-08-0]), and vinyltrimethoxysilane (VTMO, CAS reg. no. [2768-02-7]), and mixtures thereof, meaning mixtures of any of the alkylsilanes listed in this paragraph.

[0083] Single aryl-alkyl ethers, polyoxyalkylated aromatics, or alkylated aromatics may be used in the present invention. Alternatively, multiple aryl-alkyl ethers, polyoxyalkylated aromatics, and alkylated aromatics may be combined in any proportion to serve as a stabilizer blend. The stabilizer blend may contain multiple stabilizer compounds from the same class of compounds or multiple stabilizer compounds from different classes of compounds. For example, a stabilizer blend may contain 2 or more aryl-alkyl ethers, polyoxyalkylated aromatics, or alkylated aromatics, or one or more aryl-alkyl ethers, polyoxyalkylated aromatics, or alkylated aromatics in combination with one or more additional stabilizer compounds (e.g., lactones, amines, or phenols, for example).

[0084] Additionally, some of the stabilizer compounds exist as multiple configurational isomers or stereoisomers. Single isomers or multiply isomers of the same compound may be used in any proportion to prepare the stabilizer blend. Further, single or multiple isomers of a given compound may be combined in any proportion with any number of other compounds to serve as a stabilizer blend. The present invention is intended to include all single configurational isomers, single stereoisomers or any combination or mixture thereof.

[0085] Of particular note are stabilizer compositions comprising combinations of compounds that provide an unexpected level of stabilization. Certain of these combinations may serve as synergistic stabilizer compositions, that is, the compositions of compounds that augment each others' efficiency in a formulation and the stabilization obtained is larger than that expected from the sum of the contributions of the individual components. Such synergistic stabilizer compositions may comprise at least one terephthalate or mixture thereof as defined above, and any of the additional compounds selected from the group consisting of terpenes and terpenoids, fullerenes, epoxides, fluorinated epoxides, oxetanes, divinylterephthalate, and diphenylterephthalate, and mixtures thereof, meaning mixtures of any of the foregoing additional compounds with a terephthalate or mixture thereof as defined above.

[0086] A limiting factor in the effectiveness of a stabilizer composition is the consumption of stabilizer and loss of functionality over the time of active use. Of particular note, are synergistic stabilizer compositions comprising mixtures of stabilizers that include components capable of regenerating the consumed stabilizer during active use, hereinafter referred to as regenerative stabilizers. Unlike multi-functional single, large stabilizer compounds comprising multiple stabilizing functional groups, regenerative stabilizers comprising small "synergistic" stabilizers function with higher mobility and higher stabilization rates (meaning higher rates of reaction by which the stabilization is occurring). Regenerative stabilizer composition contains one or more stabilizers that can replenish itself or themselves after use, so that over long-term use, the composition's efficacy is maintained.

[0087] An example of a regenerative stabilizer is at least one terephthalate or mixture thereof as defined above, and at least one amine. Amines for inclusion in the regenerative stabilizer compositions may comprise any of the hindered amine antioxidants as described previously herein. Of particular note, are those hindered amines derived from substituted piperidine compounds, in particular derivatives of an alkyl-substituted piperidyl, piperidinyl, piperazinone, or alkoxy-piperidinyl compounds, and mixtures thereof. Representative hindered amine antioxidants are 2,2,6,6-tetramethyl-4-piperidone; 2,2,6,6-tetramethyl-4-piperidinol; bis-(1,2,2,6,6-pentamethylpiperidyl) sebacate (CAS reg. no. [41556-26-7]); di-(2,2,6,6-tetramethyl-4-piperidyl)sebacate, such as Tinuvin® 770; poly-(N-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate (CAS reg. no. [65447-77-0]), such as Tinuvin® 622LD (Ciba). Some additional hindered amine antioxidants include Tinuvin® 765 (Ciba), BLS® 1944 (Mayzo, Inc.), and BLS® 1770 (Mayzo), and mixtures thereof, including mixtures of any of the hindered amines described in this paragraph.

[0088] Another example of a regenerative stabilizer is a stabilizer which comprises at least one terephthalate or mixture thereof as defined above, combined with at least one phosphite. Of particular note are phosphites, which can be derived from substituted phosphites in particular, derivatives of alky, aryl phosphite compounds. Representative phosphites which can be used for regenerative stabilizers include (tris-(di-tert-butylphenyl) phosphite), sold under the trademark Irgafos® 168, (di-n-octyl phosphite), sold under the trademark Irgafos® OPH and (Iso-decyl diphenyl phosphite), sold under the trademark Irgafos® DDPP (all from Ciba).

[0089] Any suitable effective amount of stabilizer may be used in the compositions of the present invention. As described herein, the phrase "effective amount" refers to an amount of stabilizer of the present invention which, when added to a composition comprising at least one fluoroolefin, results in a composition that will not degrade to produce as great a reduction in refrigeration performance when in use in a cooling apparatus as compared to the composition without stabilizer. Such effective amounts of stabilizer may be determined by way of testing under the conditions of standard test ASHRAE 97-2004. In a certain embodiment of the present invention, an effective amount may be said to be that amount of stabilizer that when combined with a composition comprising at least one fluoroolefin allows a cooling apparatus utilizing said composition comprising at least one fluoroolefin to perform at the same level of refrigeration performance and cooling capacity as if a composition comprising 1,1,1,2-tetrafluoroethane (R-134a), or other standard refrigerant (R-12, R-22, R-502, R-507A, R-508, R401A, R401B, R402A, R402B, R408, R-410A, R-404A, R407C, R-413A, R-417A, R-422A, R-422B, R-422C, R-422D, R-423, R-114, R-11, R-113, R-123, R-124, R236fa, or R-245fa) depending upon what refrigerant may have been used in a similar system in the past, were being utilized as the working fluid.

[0090] Certain embodiments include effective amounts of stabilizer for use in the present invention that comprise from about 0.001 weight percent to about 10 weight percent, more preferably from about 0.01 weight percent to about 5 weight percent, even more preferably from about 0.3 weight percent to about 4 weight percent and even more preferably from about 0.3 weight percent to about 1 weight percent based on the total weight of compositions comprising at least one fluoroolefin as described herein. When a mixture of stabilizers or stabilizer blend is used, the total amount of the mixture or stabilizer blend may be present in the concentrations as described herein above.

[0091] In another embodiment, the compositions of the present invention as described above herein may further comprise at least one metal deactivator selected from the group consisting of areoxalyl bis(benzylidene)hydrazide (CAS reg. no. 6629-10-3); N,N'-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoylhydrazine) (CAS reg. no. 32687-78-8); 2,2'-oxamidobis-ethyl-(3,5-d-tert-butyl-4-hydroxyhydrocinnamate) (CAS reg. no. 70331-94-1); N,N'-(disalicylidene)-1,2-propanediamine (CAS reg. no. 94-91-1); ethylenediaminetetraacetic acid (CAS reg. no. 60-00-4) and salts thereof; triazoles; benzotriazole, 2-mercaptobenzothiazole, tolutriazole derivatives, N,N-disalicylidene-1,2-diaminopropane, and mixtures thereof, meaning mixtures of any of the foregoing metal deactivators listed in this paragraph.

[0092] In another embodiment, a stabilizer composition comprises at least one terephthalate or mixture thereof as defined above, at least one amine, and at least one metal deactivator. The metal deactivator is selected from the group consisting of areoxalyl bis(benzylidene)hydrazide; N,N'-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoylhydrazine); 2,2'-oxamidobis-ethyl-(3,5-d-tert-butyl-4-hydroxyhydrocinnamate); N,N'-(disalicylidene)-1,2-propanediamine; ethylenediaminetetraacetic acid and salts thereof; triazoles; benzotriazole, 2-mercaptobenzothiazole, tolutriazole derivatives, N,N-disalicylidene-1,2-diaminopropane, and mixtures thereof, meaning mixtures of any of the foregoing metal deactivators listed in this paragraph.

[0093] In another embodiment, a stabilizer composition comprises at least one terephthalate or mixture thereof as defined above; at least one additional compound selected from the group consisting of epoxides, oxetanes, divinyl terephthalate, and diphenyl terephthalate; and at least one metal deactivator selected from the group consisting of areoxalyl bis(benzylidene)hydrazide; N,N'-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoylhydrazine); 2,2'-oxamidobis-ethyl-(3,5-d-tert-butyl-4-hydroxyhydrocinnamate); N,N'-(disalicylidene)-1,2-propanediamine; ethylenediaminetetraacetic acid and salts thereof; triazoles; benzotriazole, 2-mercaptobenzothiazole, tolutriazole derivatives, N,N-disalicylidene-1,2-diaminopropane, and mixtures thereof, meaning mixtures of any of the foregoing metal deactivators listed in this paragraph.

[0094] In one embodiment, the compositions of the present invention may further comprise at least one additional compound selected from the group consisting of fluoroolefins (as described previously herein), hydrofluorocarbons,

hydrocarbons, dimethyl ether, CF_3I , ammonia, carbon dioxide (CO_2) and mixtures thereof, meaning mixtures of any of the additional compounds listed in this paragraph.

[0095] In one embodiment, additional compounds comprise hydrofluorocarbon (HFC) compounds. Hydrofluorocarbons comprise saturated compounds containing carbon, hydrogen, and fluorine. Of particular utility are hydrofluorocarbons having 1-7 carbon atoms and having a normal boiling point of from about -90°C to about 80°C . Hydrofluorocarbons are commercial products available from a number of sources such as E. I. du Pont de Nemours and Company, Fluoroproducts, Wilmington, DE, 19898, USA, or may be prepared by methods known in the art. Representative hydrofluorocarbon compounds include but are not limited to fluoromethane (CH_3F , HFC-41), difluoromethane (CH_2F_2 , HFC-32), trifluoromethane (CHF_3 , HFC-23), pentafluoroethane (CF_3CHF_2 , HFC-125), 1,1,2,2-tetrafluoroethane (CHF_2CHF_2 , HFC-134), 1,1,1,2-tetrafluoroethane ($\text{CF}_3\text{CH}_2\text{F}$, HFC-134a), 1,1,1-trifluoroethane (CF_3CH_3 , HFC-143a), 1,1-difluoroethane (CHF_2CH_3 , HFC-152a), fluoroethane ($\text{CH}_3\text{CH}_2\text{F}$, HFC-161), 1,1,1,2,2,3,3-heptafluoropropane ($\text{CF}_3\text{CF}_2\text{CHF}_2$, HFC-227ca), 1,1,1,2,3,3,3-heptafluoropropane ($\text{CF}_3\text{CHFCF}_3$, HFC-227ea), 1,1,2,2,3,3,3-hexafluoropropane ($\text{CHF}_2\text{CF}_2\text{CHF}_2$, HFC-236ca), 1,1,1,2,2,3-hexafluoropropane ($\text{CF}_3\text{CF}_3\text{CH}_2\text{F}$, HFC-236cb), 1,1,1,2,3,3-hexafluoropropane ($\text{CF}_3\text{CHFCHF}_2$, HFC-236ea), 1,1,1,3,3,3-hexafluoropropane ($\text{CF}_3\text{CH}_2\text{CF}_3$, HFC-236fa), 1,1,2,2,3-pentafluoropropane ($\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$, HFC-245ca), 1,1,1,2,2-pentafluoropropane ($\text{CF}_3\text{CF}_2\text{CH}_3$, HFC-245cb), 1,1,2,3,3-pentafluoropropane ($\text{CHF}_2\text{CHFCHF}_2$, HFC-245ea), 1,1,1,2,3-pentafluoropropane ($\text{CF}_3\text{CHFCH}_2\text{F}$, HFC-245eb), 1,1,1,3,3-pentafluoropropane ($\text{CF}_3\text{CH}_2\text{CHF}_2$, HFC-245fa), 1,2,2,3-tetrafluoropropane ($\text{CH}_2\text{FCF}_2\text{CH}_2\text{F}$, HFC-254ca), 1,1,2,2-tetrafluoropropane ($\text{CHF}_2\text{CF}_2\text{CH}_3$, HFC-254cb), 1,1,2,3-tetrafluoropropane ($\text{CHF}_2\text{CHFCH}_2\text{F}$, HFC-254ea), 1,1,1,2-tetrafluoropropane ($\text{CF}_3\text{CHFCH}_3$, HFC-254eb), 1,1,3,3-tetrafluoropropane ($\text{CHF}_2\text{CH}_2\text{CHF}_2$, HFC-254fa), 1,1,1,3-tetrafluoropropane ($\text{CF}_3\text{CH}_2\text{CH}_2\text{F}$, HFC-254fb), 1,1,1-trifluoropropane ($\text{CF}_3\text{CH}_2\text{CH}_3$, HFC-263fb), 2,2-difluoropropane ($\text{CH}_3\text{CF}_2\text{CH}_3$, HFC-272ca), 1,2-difluoropropane ($\text{CH}_2\text{FCHFCH}_3$, HFC-272ea), 1,3-difluoropropane ($\text{CH}_2\text{FCH}_2\text{CH}_2\text{F}$, HFC-272fa), 1,1-difluoropropane ($\text{CHF}_2\text{CH}_2\text{CH}_3$, HFC-272fb), 2-fluoropropane ($\text{CH}_3\text{CHFCH}_3$, HFC-281ea), 1-fluoropropane ($\text{CH}_2\text{FCH}_2\text{CH}_3$, HFC-281fa), 1,1,2,2,3,3,4,4-octafluorobutane ($\text{CHF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$, HFC-338pcc), 1,1,1,2,2,4,4,4-octafluorobutane ($\text{CF}_3\text{CH}_2\text{CF}_2\text{CF}_3$, HFC-338mf), 1,1,1,3,3-pentafluorobutane ($\text{CF}_3\text{CH}_2\text{CHF}_2$, HFC-365mfc), 1,1,1,2,3,4,4,5,5,5-decafluoropentane ($\text{CF}_3\text{CHFCHFCF}_2\text{CF}_3$, HFC-43-10mee), and 1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoroheptane ($\text{CF}_3\text{CF}_2\text{CHFCHFCF}_2\text{CF}_2\text{CF}_3$, HFC-63-14mee).

[0096] In another embodiment, the additional compounds comprise hydrocarbons. Hydrocarbon compounds of the present invention comprise compounds having only carbon and hydrogen. Of particular utility are compounds having 3-7 carbon atoms. Hydrocarbons are commercially available through numerous chemical suppliers. Representative hydrocarbons include but are not limited to propane, n-butane, isobutane, cyclobutane, n-pentane, 2-methylbutane, 2,2-dimethylpropane, cyclopentane, n-hexane, 2-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 3-methylpentane, cyclohexane, n-heptane, and cycloheptane.

[0097] In another embodiment, additional compounds comprise hydrocarbons containing heteroatoms, such as dimethylether (DME, CH_3OCH_3). DME is commercially available.

[0098] In another embodiment, additional compounds comprise iodotrifluoromethane (CF_3I), which is commercially available from various sources or may be prepared by methods known in the art.

[0099] In another embodiment, additional compounds comprise ammonia (NH_3), which is commercially available from various sources or may be prepared by methods known in the art.

[0100] In another embodiment, additional compounds comprise carbon dioxide (CO_2), which is commercially available from various sources or may be prepared by methods known in the art.

[0101] Of particular note are additional compounds comprising compositions including: HFC-1225ye and HFC-32; HFC-1225ye and HFC-134a; HFC-1225ye, HFC-134a, and HFC-32; HFC-1225ye and HFC-1234yf; HFC-1225ye, HFC-1234yf, and HFC-32; HFC-1225ye, HFC-1234yf, HFC-32, and CF_3I ; and HFC-1225ye, HFC-1234yf and HFC-125.

[0102] In another embodiment, additional compounds include compositions comprising fluoroolefins as disclosed in U.S. Patent Application Publication Nos. 2006/0243944 and 2006/0243945, and WO 2007/126414, are intended to be included within the scope of the present invention.

[0103] In one embodiment, compositions of the present invention may further comprise at least one lubricant. Lubricants of the present invention comprise those suitable for use with refrigeration or air-conditioning apparatus. Among these lubricants are those conventionally used in compression refrigeration apparatus utilizing chlorofluorocarbon refrigerants. Such lubricants and their properties are discussed in the 1990 ASHRAE Handbook, Refrigeration Systems and Applications, chapter 8, titled "Lubricants in Refrigeration Systems", pages 8.1 through 8.21, herein incorporated by reference. Lubricants of the present invention may comprise those commonly known as "mineral oils" in the field of compression refrigeration lubrication. Mineral oils comprise paraffins (i.e. straight-chain and branched-carbon-chain, saturated hydrocarbons), naphthenes (i.e. cyclic or ring structure saturated hydrocarbons, which may be paraffins) and aromatics (i.e. unsaturated, cyclic hydrocarbons containing one or more rings characterized by alternating double bonds). Lubricants of the present invention further comprise those commonly known as "synthetic oils" in the field of compression refrigeration lubrication. Synthetic oils comprise alkylaryls (i.e. linear and branched alkyl alkylbenzenes), synthetic paraffins and naphthenes, silicones, and poly-alpha-olefins. Representative conventional lubricants of the present invention are the

commercially available BVM 100 N (paraffinic mineral oil sold by BVA Oils), naphthenic mineral oil commercially available under the trademark from Suniso® 3GS and Suniso® 5GS by Crompton Co., naphthenic mineral oil commercially available from Pennzoil under the trademark Sontex® 372LT, naphthenic mineral oil commercially available from Calumet Lubricants under the trademark Calumet® RO-30, linear alkylbenzenes commercially available from Shrieve Chemicals under the trademarks Zerol® 75, Zerol® 150 and Zerol® 500 and branched alkylbenzene, sold by Nippon Oil as HAB 22.

[0104] In another embodiment, lubricants of the present invention further comprise those which have been designed for use with hydrofluorocarbon refrigerants and are miscible with refrigerants of the present invention under compression refrigeration and air-conditioning apparatus' operating conditions. Such lubricants and their properties are discussed in "Synthetic Lubricants and High-Performance Fluids", R. L. Shubkin, editor, Marcel Dekker, 1993. Such lubricants include, but are not limited to, polyol esters (POEs) such as Castrol® 100 (Castrol, United Kingdom), polyalkylene glycols (PAGs) such as RL-488A from Dow (Dow Chemical, Midland, Michigan), and polyvinyl ethers (PVEs).

[0105] Lubricants of the present invention are selected by considering a given compressor's requirements and the environment to which the lubricant will be exposed.

[0106] The compositions of the present invention may be prepared by any convenient method to combine the desired amount of the individual components. A preferred method is to weigh the desired component amounts and thereafter combine the components in an appropriate vessel. Agitation may be used, if desired.

[0107] The present invention further relates to a method for stabilizing a composition comprising at least one fluoroolefin, said method comprising adding an effective amount of a stabilizer comprising at least one terephthalate selected from divinyl terephthalate and diphenyl terephthalate to the composition comprising at least one fluoroolefin.

[0108] The present invention further relates to a process for producing cooling comprising condensing a composition comprising at least one fluoroolefin and an effective amount of stabilizer comprising at least one terephthalate as defined above, in the vicinity of a body to be cooled.

[0109] A body to be cooled may be any space, location or object requiring refrigeration or air-conditioning. In stationary applications the body may be the interior of a structure, i.e. residential or commercial, or a storage location for perishables, such as food or pharmaceuticals. For mobile refrigeration applications the body may be incorporated into a transportation unit for the road, rail, sea or air. Certain refrigeration systems operate independently with regards to any moving carrier, these are known as "intermodal" systems. Such intermodal systems include "containers" (combined sea/land transport) as well as "swap bodies" (combined road and rail transport).

[0110] The present invention further relates to a process for producing heat comprising condensing a composition comprising at least one fluoroolefin and an effective amount of stabilizer comprising at least one terephthalate as defined above, in the vicinity of a body to be heated, and thereafter evaporating said composition.

[0111] A body to be heated may be any space, location or object requiring heat. These may be the interior of structures either residential or commercial in a similar manner to the body to be cooled. Additionally, mobile units as described for cooling may be similar to those requiring heating. Certain transport units require heating to prevent the material being transported from solidifying inside the transport container.

[0112] It is not uncommon for air to leak into a refrigeration, air-conditioning or heat pump system. The oxygen in the air may lead to oxidation of certain components of the system including the working fluid. Thus, in another embodiment, also disclosed is a method for reducing degradation of a composition comprising at least one fluoroolefin, wherein said degradation is caused by the presence of inadvertent air; for example in a refrigeration, air-conditioning or heat pump system, said method comprising adding an effective amount of stabilizer comprising at least one terephthalate as defined above, to the composition comprising at least one fluoroolefin.

[0113] In one embodiment, the present invention provides a composition comprising at least one fluoroolefin and a stabilizer comprising an effective amount of at least one metal salt or mixture thereof. Metal salts of the present invention may be metal oxides, bicarbonates, carbonates, acetates, halides, oxalates, sulfates, silicates, phosphates, molybdates, hydroxides, borates or pyrophosphates. The metals for the metal salt stabilizers may be manganese, copper (I and II), titanium, cobalt, cerium, potassium, sodium, calcium, iron, rubidium, magnesium, antimony, molybdenum and others. Representative metal salts include but are not limited to, titanium dioxide (TiO_2), calcium carbonate (CaCO_3), sodium sulfate (Na_2SO_4), aluminas, aluminum silicates, clays, sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$), cerium acetate ($\text{CH}_3\text{CO}_2\text{Na}$), potassium acetate ($\text{CH}_3\text{CO}_2\text{K}$), potassium carbonate (K_2CO_3), iron (II) carbonate (FeCO_3), sodium carbonate (Na_2CO_3), ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$), sodium bicarbonate (NaHCO_3), potassium bicarbonate, (KHCO_3), ammonium phosphate ($(\text{NH}_4)_3\text{PO}_4$), potassium nitrate (KNO_3), sodium chloride (NaCl), potassium chloride (KCl), cobalt chloride (CoCl_2), rubidium chloride (RbCl), titanium chloride (TiCl_4), sodium bromide (NaBr), potassium bromide (KBr), rubidium bromide (RbBr), potassium iodide (KI), rubidium iodide (RbI), magnesium hydroxide ($\text{Mg}(\text{OH})_2$), aluminum hydroxide ($\text{Al}(\text{OH})_3$), zinc borate ($3\text{ZnO} \cdot 2\text{B}_2\text{O}_3$), zinc oxide (ZnO), zinc molybdate (ZnMoO_4), calcium molybdate (CaMoO_4), copper oxides, (Cu_2O and CuO), and antimony oxides, including but not limited to antimony trioxide (Sb_2O_3) and antimony pentoxide (Sb_2O_5), and others.

[0114] In one embodiment, the stabilizer compositions comprise at least one metal salts. In another embodiment, the additional stabilizers comprise metal salts. In another embodiment, metal salts serve as a component of a regenerative

stabilizer blend.

EXAMPLE

Refrigeration system chemical stability

[0115] A chemical stability test is run under conditions described in ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) Standard 97-2004 to determine chemical stability of the stabilized compositions of the present invention as compared to compositions with no stabilizers.

[0116] The procedure is given here:

1. Metal coupons of copper, aluminum and steel are placed in thick walled glass tubes.
2. Working fluid samples, including lubricant, are prepared with and without stabilizers, and optionally with 2 volume % air added to the tube.
3. Samples are added to the glass tubes as described in the standard.
4. The tubes are sealed with a glass blowing torch.
5. The sealed tubes are heated in an oven for 14 days at the specified temperature.
6. After 14 days, the sealed tubes are removed from the oven and examined for metal/liquid appearance, proper volume of liquid, appearance of glass, and absence of extraneous materials such as metal fines.
7. Ratings are assigned to each sample based upon the following criteria (per industry practice):

- 1 = light changes on coupons and liquids;
- 2 = light to moderate changes on coupons or liquids;
- 3 = moderate to significant changes on coupons or liquids;
- 4 = severe changes on coupons or liquids;
- 5 = extreme changes on coupons or liquids, i.e. black liquid or coked with many deposits.

Table 4 lists estimated results for stabilizers of the present invention as compared to unstabilized compositions. Ucon® PAG 488 is a trademark for a polyalkylene glycol lubricant commercially available from The Dow Chemical Company. The lubricant Ucon® PAG 488 is combined with the working fluid as set forth in Table 4 below to produce a composition that was 50 wt% working fluid and 50 wt% lubricant.

TABLE 4

<u>Working fluid</u>	<u>Lubricant</u>	<u>Stabilizer</u>	<u>Stabilizer (wt% in refrig/ lubricant mixture)</u>	<u>With 2 vol% Air</u>	<u>Temp (°C)</u>	<u>Rating</u>
HFC-1225ye	PAG 488	None	0	yes	175	4
HFC-1225ye	PAG 488	None	0	no	175	2
HFC-1225ye	PAG 488	Divinyl terephthalic acid	2	yes	175	2
HFC-1225ye	PAG 488	Divinyl terephthalic acid	2	no	175	1

Estimates indicate improved chemical stability in the presence of stabilizers with and without air present.

Claims

1. A composition comprising:

- a) at least one fluoroolefin; and
- b) an effective amount of a stabilizer comprising at least one terephthalate selected from divinyl terephthalate

and diphenyl terephthalate.

2. The composition of claim 1 further comprising at least one additional compound selected from the group consisting of fluoroolefins, hydrofluorocarbons, hydrocarbons, dimethyl ether, CF_3I , carbon dioxide, ammonia, and mixtures thereof.
3. The composition of claim 1 further comprising a lubricant selected from the groups consisting of mineral oils, alkylbenzenes, poly-alpha-olefins, silicone oils, polyoxyalkylene glycol ethers, polyol esters, polyvinylethers, and mixtures thereof.
4. A method for stabilizing a composition comprising at least one fluoroolefin, said method comprising adding an effective amount of a stabilizer comprising at least one terephthalate selected from divinyl terephthalate and diphenyl terephthalate to the composition comprising at least one fluoroolefin.
5. A process for producing cooling comprising condensing the composition of claim 1 and thereafter evaporating said composition in the vicinity of a body to be cooled.
6. A process for producing heat comprising condensing the composition of claim 1 in the vicinity of a body to be heated, and thereafter evaporating said composition.
7. A method for reducing degradation of a composition comprising at least one fluoroolefin, wherein said degradation is caused by the presence of inadvertent air in a refrigeration, air-conditioning or heat pump system, said method comprising adding an effective amount of at least one terephthalate selected from divinyl terephthalate and diphenyl terephthalate to the composition comprising at least one fluoroolefin.

Patentansprüche

1. Zusammensetzung, umfassend:

- a) mindestens ein Fluorolefin; und
- b) eine wirksame Menge eines Stabilisators, umfassend mindestens ein Terephthalat, ausgewählt aus Divinylterephthalat und Diphenylterephthalat.

2. Zusammensetzung nach Anspruch 1, ferner umfassend mindestens eine zusätzliche Verbindung, ausgewählt aus der Gruppe, bestehend aus Fluorolefinen, Fluorkohlenwasserstoffen, Kohlenwasserstoffen, Dimethylether, CF_3I , Kohlendioxid, Ammoniak und Gemischen davon.
3. Zusammensetzung nach Anspruch 1, ferner umfassend ein Schmiermittel, ausgewählt aus der Gruppe, bestehend aus Mineralölen, Alkylbenzolen, Polyalphaolefinen, Silikonölen, Polyoxyalkylenglykolethern, Polyolestern, Polyvinylethern und Gemischen davon.
4. Verfahren zum Stabilisieren einer mindestens ein Fluorolefin umfassenden Zusammensetzung, wobei das Verfahren Zugeben einer wirksamen Menge eines Stabilisators, der mindestens ein Terephthalat, ausgewählt aus Divinylterephthalat und Diphenylterephthalat, zu der mindestens ein Fluorolefin umfassenden Zusammensetzung umfasst.
5. Prozess zum Erzeugen von Kühlung, umfassend Kondensieren der Zusammensetzung nach Anspruch 1 und danach Verdampfen der Zusammensetzung in der Nähe eines zu kühlenden Körpers.
6. Prozess zum Erzeugen von Wärme, umfassend Kondensieren der Zusammensetzung nach Anspruch 1 in der Nähe eines zu erwärmenden Körpers, und danach Verdampfen der Zusammensetzung.
7. Verfahren zum Verringern des Abbaus einer mindestens ein Fluorolefin umfassenden Zusammensetzung, wobei der Abbau durch das Vorhandensein ungewollter Luft in einem Kühl-, Klimatisierungs- oder Wärmepumpensystem verursacht wird, wobei das Verfahren Zugeben einer wirksamen Menge von mindestens einem Terephthalat, ausgewählt aus Divinylterephthalat und Diphenylterephthalat, zu der mindestens ein Fluorolefin umfassenden Zusammensetzung umfasst.

Revendications

1. Composition comprenant:

- a) au moins une fluorooléfine; et
b) une quantité efficace d'un stabilisant comprenant au moins un téréphtalate choisi parmi le divinyltéréphtalate et le diphényltéréphtalate.

2. Composition selon la revendication 1, comprenant en outre au moins un composé supplémentaire choisi dans le groupe constitué de fluorooléfines, d'hydrofluorocarbures, d'hydrocarbures, de diméthyléther, de CF₃I, de dioxyde de carbone, d'ammoniaque et de mélanges de ceux-ci.

3. Composition selon la revendication 1, comprenant en outre un lubrifiant choisi dans le groupe constitué d'huiles minérales, d'alkylbenzènes, de poly-alpha-oléfines, d'huiles de silicone, d'éthers de polyoxyalkylène glycol, d'esters de polyol, de polyvinyléthers et de mélanges de ceux-ci.

4. Méthode pour la stabilisation d'une composition comprenant au moins une fluorooléfine, ladite méthode comprenant l'ajout d'une quantité efficace d'un stabilisant comprenant au moins un téréphtalate choisi parmi le divinyltéréphtalate et le diphényltéréphtalate à la composition comprenant au moins une fluorooléfine.

5. Procédé pour la production de réfrigération comprenant la condensation de la composition selon la revendication 1 et par la suite l'évaporation de ladite composition dans le voisinage d'un corps à réfrigérer.

6. Procédé pour la production de chaleur comprenant la condensation de la composition selon la revendication 1 dans le voisinage d'un corps à chauffer et par la suite l'évaporation de ladite composition.

7. Méthode pour la réduction de la dégradation d'une composition comprenant au moins une fluorooléfine, dans laquelle ladite dégradation est entraînée par la présence d'air par inadvertance dans une réfrigération, un conditionnement d'air ou un système de pompe à chaleur, ladite méthode comprenant l'ajout d'une quantité efficace d'au moins un téréphtalate choisi parmi le divinyltéréphtalate et le diphényltéréphtalate ou un mélange de ceux-ci avec au moins un parmi l'acide ascorbique et le nitrométhane à la composition comprenant au moins une fluorooléfine.

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